A Mechanistic Investigation of Enantioconvergent Kumada Reactions of Racemic α-Bromoketones Catalyzed by a Nickel/Bis(oxazoline) Complex

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Supporting Information

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I. General Information

Materials. The following reagents were purchased from commercial suppliers and used as received: $Ni(cod)_2$ (Strem), $NiBr_2(dme)$ (Sigma-Aldrich), PhMgBr (3.0 M in Et_2O, Sigma-Aldrich). (*R*,*R*)-Ph-BOX and (*S*,*S*)-Ph-BOX ligands were prepared according to a literature procedure;[1] (*R*,*R*)-Ph-BOX was used in experiments, unless otherwise noted. (±)-2-Bromopropiophenone was purchased from Sigma-Aldrich and distilled before use. DME, THF, toluene, Et_2O, and *n*-pentane were sparged with dry argon and dried via a solvent purification system comprised of columns packed with neutral alumina.

Chromatography. Gas chromatography data were collected on an Agilent 6890N GC system with an FID detector. Yields by GC were determined using calibration curves, using *n*-dodecane as an internal standard. Analysis of enantioenriched organic compounds was conducted on an Agilent 1100 series HPLC using Daicel CHIRALCEL® or Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm).

Elemental analysis. Elemental analyses were carried out at the Beckman Institute at Caltech with a PerkinElmer 2400 Series II CHN Elemental Analyzer or at Midwest Microlab.

Mass spectrometry. ESI-MS experiments were collected using an Agilent 6200 Series TOF MS with Agilent G1978A multimode source in electrospray ionization mode. GC-MS data were collected on an Agilent 7890A GC system with an Agilent 5975C mass detector.

Spectroscopy. X-Band continuous-wave EPR measurements were conducted on a Bruker EMX spectrometer with the sample in a frozen solvent glass at 77 K. Simulation of EPR spectra was accomplished using the EasySpin package.[2]

UV-vis spectra were collected on a Cary 50 UV-vis spectrometer using a 10 mm path-length quartz cuvette equipped with a puncturable screw cap. Variable-temperature measurements employed a Unisoku CoolSpek cryostat.

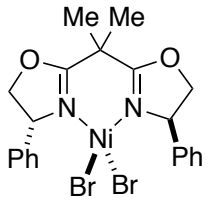
^1H and ^{13}C NMR spectra were collected on a 400 MHz Varian spectrometer with a broadband cryoprobe. Variable-temperature multi-nuclear NMR data were collected on a 500 MHz Varian spectrometer.

FT-IR measurements of organic compounds were carried out on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory. FT-IR measurements of nickel complexes were conducted in a nitrogen-filled glovebox using a Bruker Alpha FT-IR spectrometer equipped with a single-reflection diamond ATR module.

X-ray crystallography. Single-crystal diffraction data were collected at the Beckman Institute at Caltech with a Bruker SMART 1000 CCD diffractometer with filtered Mo–Kα radiation.

II. Synthesis

These yields have not been optimized.



1

$Ni^{II}Br_2$(Ph-BOX) (1).

Method A: From $NiBr_2$(dme). (*R*,*R*)-Ph-BOX (0.668 g, 2.00 mmol) and $NiBr_2$(dme) (0.617 g, 2.00 mmol) were weighed in the air and added to a 100 mL round bottom flask. Anhydrous THF (50 mL) was added, resulting in an immediate color change to purple. The mixture was heated at 65 °C for 4 h, and then it was filtered through Celite (dried at 140 °C for 3 h prior to use) packed on a medium-size fritted filter. The Celite was washed with THF (3 mL × 3), the filtrates were combined, and the volatiles were removed under reduced pressure, affording a magenta solid. The resulting magenta solid was collected on a medium-size fritted filter, washed with anhydrous Et_2O (5 mL × 3), and dried under reduced pressure. Yield: 1.04 g (94%). The product was stored in a glovebox.

Method B: From $Ni(cod)_2$ (eq 6). Bromobenzene (0.188 g, 1.20 mmol) was added to a solution of (*R*,*R*)-Ph-BOX (0.110 g, 0.330 mmol) and $Ni(cod)_2$ (0.083 g, 0.300 mmol) in toluene (5 mL). The mixture was left undisturbed for 24 h, resulting in the precipitation of a magenta crystalline solid. The solid was washed with *n*-pentane (3 mL × 3) and dried under reduced pressure. Yield: 0.130 g (78%). The biphenyl byproduct in the supernatant of the reaction was identified by GC-MS.

This complex is not sensitive to dry air, but it degrades slowly in the presence of moisture.

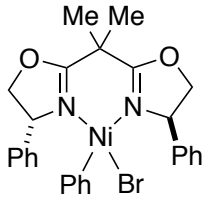
Crystals suitable for X-ray crystallography were obtained by DME/*n*-pentane vapor diffusion at room temperature.

^{1}H NMR (400 MHz, THF-d_8, 300 K) δ 64.04 (br, 2H), 18.89 (s, 2H), 17.17 (br, 4H), 9.31 (br, 2H), 9.17 (br, 4H), 5.93 (br, 2H), 1.23 (br, 6H). This is a high-spin Ni(II) complex.

Because the sample is paramagnetic, the ^{13}C NMR signals are too weak to be observed.

FT-IR (solid) 1651, 1477, 1452, 1425, 1389, 1231, 1137, 979, 758, 743, 697 cm^{-1}.

Elemental analysis calculated for $C_{21}H_{22}Br_2N_2NiO_2$: C, 45.62; H, 4.01; N, 5.07. Found: C, 45.73; H, 4.00; N, 5.04.



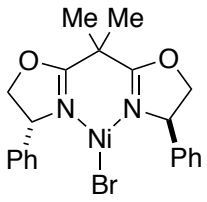
2

Ni^{II}PhBr(Ph-BOX) (2) (eq 7). *n*-Pentane (50 mL) was added to a 100 mL round bottom flask that contained (*R*,*R*)-Ph-BOX (0.334 g, 1.00 mmol) and Ni(cod)$_2$ (0.275 g, 1.00 mmol). The resulting yellow mixture was stirred vigorously at room temperature for 1 h, and then it was filtered through an acrodisc. To the filtrate was added bromobenzene (0.173 g, 1.10 mmol), and the resulting mixture was stirred vigorously for 3 h, during which time an orange precipitate formed. The orange powder was collected on a medium-porosity fritted filter, washed with *n*-pentane (3 mL × 3), and dried under reduced pressure. Yield: 0.376 g (68%).

This complex is sensitive to air and to moisture in the solid state, and it decomposes rapidly at room temperature in DME.

FT-IR (solid) 1653, 1494, 1474, 1229, 1131, 935, 744, 729, 694 cm^{-1}.

Elemental analysis calculated for $C_{27}H_{27}BrN_2NiO_2$: C, 58.95; H, 4.95; N, 5.09. Found: C, 58.46; H, 5.38; N, 5.17.



3

Ni^{I}Br(Ph-BOX) (3) (eq 8). THF (5 mL, pre-cooled to −40 °C) was added to a 20 mL vial that contained Ni^{II}PhBr(Ph-BOX) (**2**; 0.055 g, 0.100 mmol, pre-cooled to −40 °C), resulting in a clear orange solution. The orange solution was layered with *n*-pentane (5 mL, pre-cooled to −40 °C) and stored at −40 °C for 1 day, resulting in the formation of a yellow solid. The yellow solid was collected on a medium-porosity fritted filter, washed with cold *n*-pentane (−40 °C; 1 mL), and dried under reduced pressure. Yield: 0.031 g (66%).

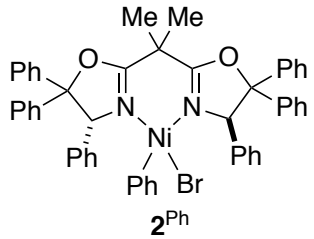
This complex is sensitive to air and to moisture in the solid state, and it decomposes at room temperature in solution.

Crystals suitable for X-ray crystallography were obtained by THF/*n*-pentane layering at −78 °C.

^{1}H NMR (THF-d_8, 500 MHz, 243 K) δ 7.18 (br). This is a paramagnetic Ni(I) complex.

FT-IR (solid) 1656, 1476, 1454, 1384, 1229, 1122, 752, 698 cm^{-1}.

Elemental analysis calculated for $C_{21}H_{22}BrN_2NiO_2 \cdot C_4H_8O$: C, 55.08; H, 5.55; N, 5.14. Found: C, 55.12; H, 5.06; N, 5.55.



2^{Ph}

$Ni^{II}PhBr(Ph\text{-}BOX^{Ph})$ (2^{Ph}) (eq 7). *n*-Pentane (20 mL) was added to a 20 mL vial that contained (*R*,*R*)-Ph-BOX^{Ph} (0.128 g, 0.200 mmol) and $Ni(cod)_2$ (0.055 g, 0.200 mmol). The resulting yellow solution was stirred at room temperature for 10 min, and then it was filtered through an acrodisc into a 20 mL vial that contained bromobenzene (0.035 g, 0.22 mmol). The mixture was stirred for 2 h, resulting in the precipitation of an orange solid. The orange solid was collected on a medium-porosity fritted filter, washed with *n*-pentane (3 mL × 3), and dried under reduced pressure. Yield: 0.131 g (77%).

This complex is sensitive to air and to moisture in the solid state, and it decomposes rapidly when stored as a solution in DME above −10 °C.

Crystals suitable for X-ray crystallography were obtained by THF/*n*-pentane layering at −40 °C. Both the THF and the *n*-pentane were pre-cooled to −40 °C before use in the recrystallization.

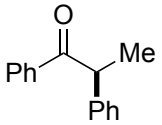
^{1}H NMR (THF-d_8, 500 MHz, 243 K) δ 7.83 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.39 (m, H), 7.37 – 7.25 (m, 2H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.02 – 6.77 (m, 18H), 6.72 – 6.70 (m, 2H), 6.68 (s, 1H), 6.34 (t, *J* = 7.5 Hz, 1H), 6.06 (s, 1H), 1.95 (s, 3H), 1.91 (s, 3H).

FT-IR (solid) 1649, 1447, 1137, 971, 745, 732, 692, 620 cm^{-1}.

Elemental analysis calculated for $C_{51}H_{43}BrN_2NiO_2$: C, 71.69; H, 5.07; N, 3.28. Found: C, 71.40; H, 5.15; N, 3.21.

III. Model Catalyzed Reaction (eq 3)

Model catalyzed reaction. In a nitrogen-filled glovebox, a solution of PhMgBr in Et_2O (3.0 M; 37 μL, 0.11 mmol) was added to DME (8.0 mL) in a 20 mL vial equipped with a stir bar and fitted with a PTFE septum cap. This mixture was stirred until it was homogeneous, and then the vial was removed from the glovebox and cooled to −60 °C. In a nitrogen-filled glovebox, $Ni^{II}Br_2$(Ph-BOX) (**1**; 3.9 mg, 0.0070 mmol) and DME (2.0 mL) were added to a 4.0 mL vial equipped with a stir bar. The reaction mixture was stirred for 5 min until it was homogeneous. Next, 2-bromopropiophenone (15 μL, 0.10 mmol) was added. The mixture was stirred at room temperature for 5 min, and then the resulting purple solution was removed from the glovebox and added dropwise over 30 s to the −60 °C solution of PhMgBr. The resulting orange-yellow solution was stirred at −60 °C for 20 h, and then the reaction was quenched by the addition of ethanol (1.0 mL). The resulting mixture was analyzed via GC and chiral HPLC.



(*S*)-1,2-Diphenylpropan-1-one (eq 3). The title compound was synthesized from (±)-2-bromo-1-phenyl-1-propanone and PhMgBr using the above procedure ($Ni^{II}Br_2$((*R*,*R*)-Ph-BOX)). The product was purified by chromatography on silica gel (3% EtOAc/hexanes), which furnished a colorless oil in 75% yield, 90% ee.

A second run conducted with $Ni^{II}Br_2$((*S*,*S*)-Ph-BOX) provided the product in 74% yield, –90% ee.

The characterization data are consistent with our previous report.[3]

Time-course experiment (Figure 3). In a nitrogen-filled glovebox, a solution of PhMgBr in Et_2O (3.0 M; 37 μL, 0.11 mmol) was added to DME (8.0 mL) in a 20 mL vial fitted with a PTFE septum cap. This mixture was stirred until it was homogeneous, and then the vial was removed from the glovebox and cooled to −60 °C. A solution of $Ni^{II}Br_2$(Ph-BOX) (**1**; 3.9 mg, 0.0070 mmol), 2-bromopropiophenone (15 μL, 0.10 mmol), and *n*-dodecane (23 μL, 0.10 mmol) in DME (2.0 mL) was added to this vial via syringe over 30 s, with stirring. The puncture was then sealed with Dow Corning grease. At each indicated time point, an aliquot (0.5 mL) of the reaction was removed, quenched with EtOH (0.1 mL), and subjected to analysis via GC and chiral HPLC.

The same experiment performed using a cold well (–60 °C) in a nitrogen-filled glovebox afforded consistent results.

Monitoring via EPR spectroscopy. In a nitrogen-filled glovebox, a solution of PhMgBr in Et_2O (3.0 M; 37 μL, 0.11 mmol) was added to DME (8.0 mL) in a 20 mL vial fitted with a PTFE septum cap. This mixture was stirred until it was homogeneous, and then it was cooled to −60 °C. A solution that contained $Ni^{II}Br_2$(Ph-BOX) (**1**; 3.9 mg, 0.0070 mmol), 2-bromopropiophenone (15 μL, 0.10 mmol), and *n*-dodecane (23 μL, 0.10 mmol) in DME (2.0 mL) was added via syringe over 30 s, with stirring.

At each indicated time point, an aliquot (0.3 mL) of the reaction mixture was transferred via syringe to an EPR tube (pre-cooled to −60 °C) equipped with a rubber septum sealed under N_2. The puncture in the rubber septum was sealed with Dow Corning grease. The EPR tube was then promptly frozen with liquid nitrogen and subjected to EPR analysis at 77 K.

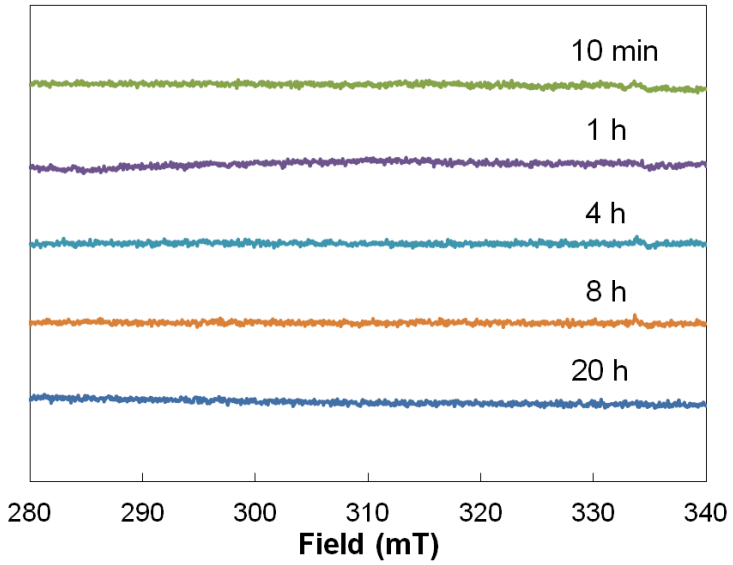


Figure S–1. X-band EPR spectra of the coupling reaction after 10 min, 1 h, 4 h, 8 h, and 20 h. The spectra were collected at ν = 9.4 GHz, 2 mW power, and a modulation amplitude of 2 G.

Monitoring via UV-vis spectroscopy. In a nitrogen-filled glovebox, a solution of PhMgBr in Et_2O (3.0 M; 15 μL, 0.044 mmol) was added to DME (3.2 mL) in a quartz cuvette. The cuvette was then sealed with a puncturable screw cap and cooled to –60 °C. A solution that contained $Ni^{II}Br_2$(Ph-BOX) (**1**; 1.5 mg, 0.0028 mmol), 2-bromopropiophenone (6.0 μL, 0.040 mmol), and *n*-dodecane (9.0 μL, 0.040 mmol) in DME (0.8 mL) was added via syringe over 10 s, with stirring. Spectra were collected every 5 minutes.

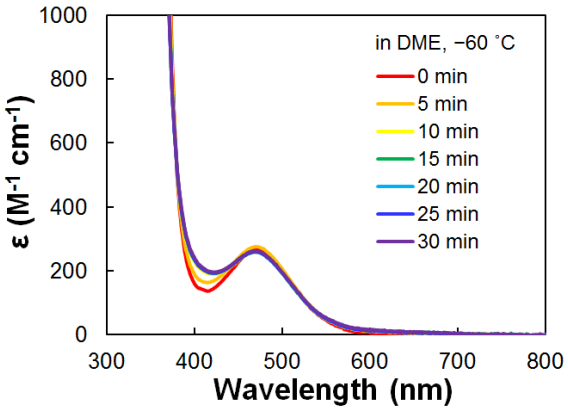
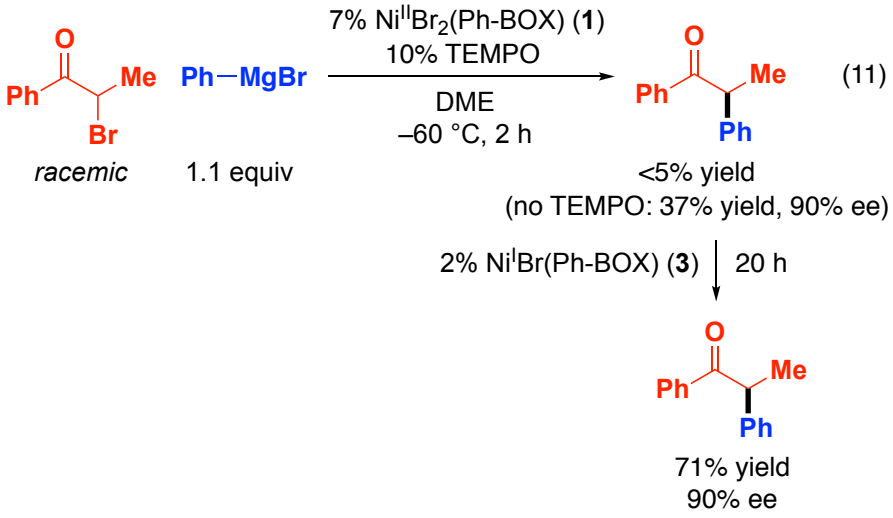


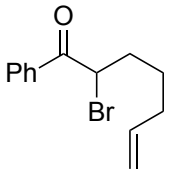
Figure S–2. UV-vis spectra (DME, –60 °C) of the coupling reaction. The absorption from PhMgBr has been subtracted.



TEMPO inhibition and reactivation (eq 11). In a nitrogen-filled glovebox, a solution of PhMgBr in Et_2O (3.0 M; 37 μL, 0.11 mmol) was added to DME (8.0 mL) in a 20 mL vial fitted with a PTFE septum cap. This mixture was stirred until it was homogeneous, and then it was cooled to −60 °C. A solution that contained $Ni^{II}Br_2$(Ph-BOX) (**1**; 3.9 mg, 0.0070 mmol), 2-bromopropiophenone (15 μL, 0.10 mmol), TEMPO (1.5 mg, 0.010 mmol), and *n*-dodecane (23 μL, 0.10 mmol) in DME (2.0 mL) was added via syringe over 30 s, with stirring. An aliquot (0.5 mL) was taken after 2 h, quenched with EtOH, and analyzed via GC.

A solution that contained $Ni^{I}Br$(Ph-BOX) (**3**; 0.0020 mmol) in DME (0.5 mL) at –60 °C was added via pipette. After stirring at –60 °C for 20 h, the reaction was quenched with EtOH and analyzed via GC and chiral HPLC.

IV. Radical-Probe Experiments



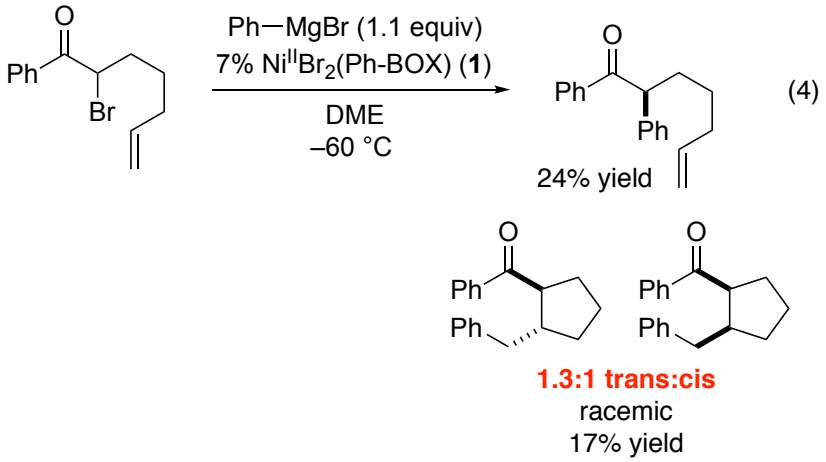
2-Bromo-1-phenylhept-6-en-1-one. 1-Phenylhept-6-en-one (1.22 g, 6.5 mmol)[4] was added to a solution that contained LDA (1.07 g, 10.0 mmol) in THF (5 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 15 min, and then Me_3SiCl (1.41 g, 13.0 mmol) was added. The mixture was allowed to warm to room temperature, and then it was stirred for 2 h. Next, the volatiles were removed, and CH_2Cl_2 (10 mL) and then *N*-bromosuccinimide (1.39 g, 7.8 mmol; added portionwise) were added. The reaction mixture was stirred for 16 h, and then the reaction was quenched with water (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. The product was purified via flash chromatography on silica gel (eluted with CH_2Cl_2:hexanes 3:7; colorless oil, 1.15 g, 66% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 – 8.00 (m, 2H), 7.63 – 7.57 (m, 1H), 7.52 – 7.47 (m, 2H), 5.85 – 5.75 (m, 1H), 5.15 (dd, *J* = 7.9, 6.4 Hz, 1H), 5.08 – 5.01(m, 1H), 5.00 – 4.96 (m, 1H), 2.27 – 2.09 (m, 4H), 1.70 – 1.46 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.3, 138.0, 134.6, 133.9, 129.0, 128.9, 115.5, 47.2, 33.3, 33.0, 26.9.

FT-IR (film) 3074, 2932, 1687, 1596, 1448, 1279, 1249, 914, 704, 686 cm^{-1}.

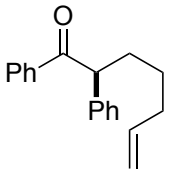
MS (ESI) m/z ([M+H]$^+$) calcd for $C_{13}H_{16}BrO$: 267, found 267.



Cyclization study (eq 4). In a nitrogen-filled glovebox, a solution of PhMgBr in Et_2O (3.0 M; 37 μL, 0.11 mmol) was added to DME (8.0 mL) in a 20 mL vial equipped with a stir bar and fitted with a PTFE septum cap. This mixture was stirred until it was

homogeneous, and then it was removed from the glovebox and cooled to −60 °C. In a nitrogen-filled glovebox, $Ni^{II}Br_2$(Ph-BOX) (**1**; 3.9 mg, 0.0070 mmol) and DME (1.0 mL) were added to a 4.0 mL vial equipped with a stir bar. The reaction mixture was stirred for 5 min, at which time it was homogeneous. Next, 2-bromo-1-phenylhept-6-en-one (27 mg, 0.10 mmol) in DME (1.0 mL) was added. The mixture was stirred at room temperature for 5 min, and then the vial was removed from the glovebox, and the purple solution was added dropwise over 30 s to the −60 °C solution of PhMgBr. The resulting orange-yellow solution was stirred at −60 °C for 20 h, and then the reaction was quenched with ethanol (1.0 mL). The resulting mixture was filtered through a pad of silica gel (height: 3.0 cm). The silica was washed with Et_2O (3 mL × 3), and then the combined filtrates were concentrated and dried under vacuum. The residue was subjected to analysis via ^{1}H NMR spectroscopy (with 1,1,2,2-tetrachloroethane as an internal standard) and chiral HPLC.

The uncyclized (**U**) product was formed in 24% yield (75% ee), the trans cyclized product (**C**) was formed in 9% yield, and the cis cyclized product (**C**) was formed in 8% yield.



(*S*)-1,2-Diphenyl-phenylhept-6-en-one. Colorless oil.

The ee was determined via HPLC on a CHIRALCEL AD-H column (1% ^{i}PrOH/hexanes, 1.0 mL/min) with t_r = 12.1 (major), 13.7 min (minor).

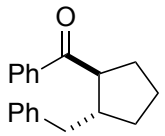
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 – 7.80 (m, 2H), 7.35 – 7.30 (m, 1H), 7.26 – 7.20 (m, 2H), 7.19 – 7.11 (m, 4H), 7.08 – 7.02 (m, 1H), 5.69 − 5.56 (m, 1H), 4.88 – 4.81 (m, 1H), 4.81 − 4.76 (m, 1H), 4.41 (t, *J* = 8.0 Hz, 1H), 2.11 – 2.00 (m, 1H), 2.00 – 1.85 (m, 2H), 1.77 – 1.65 (m, 1H), 1.36 – 1.11 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.1, 139.8, 138.6, 137.0, 133.0, 129.0, 128.8, 128.6, 128.3, 127.1, 114.8, 53.7, 33.9, 33.7, 27.1.

FT-IR (film) 3063, 2929, 1682, 1598, 1448, 1226, 912, 755, 698 cm^{-1}.

MS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{21}O$: 265.1587, found 265.1585.

$[\alpha]^{22}_D$ = 103° (c = 1.0, $CHCl_3$); 75% ee.



***trans*-(2-Benzylcyclopentyl)(phenyl)methone.** Colorless oil.

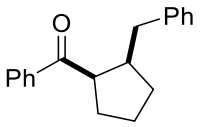
The ee was determined via HPLC on a CHIRALCEL AD-H column (1% ^{i}PrOH/hexanes, 1.0 mL/min) with t_r = 12.8, 16.4 min (racemic).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 – 7.77 (m, 2H), 7.56 – 7.49 (m, 1H), 7.44 – 7.38 (m, 2H), 7.25 – 7.20 (m, 2H), 7.18 – 7.10 (m, 3H), 3.46 (dt, *J* = 9.2, 6.8 Hz, 1H), 2.80 – 2.70 (m, 2H), 2.62 – 2.57 (m, 1H), 2.15 – 2.03 (m, 1H), 1.90 – 1.65 (m, 4H), 1.45 – 1.35 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.9, 141.0, 137.1, 132.7, 129.0, 128.4, 128.3, 128.2, 125.9, 51.8, 44.7, 41.0, 32.1, 30.8, 24.6.

FT-IR (film) 3026, 2952, 1678, 1448, 1221, 1002, 746, 700 cm^{-1}.

MS (ESI) m/z ([M+H]$^+$) calcd for $C_{19}H_{21}O$: 265.1587, found 265.1588.



***cis*-(2-Benzylcyclopentyl)(phenyl)methone.** Colorless oil.

The ee was determined via HPLC on a CHIRALCEL OJ-H column (1% ^{i}PrOH/hexanes, 1.0 mL/min) with t_r = 12.9, 15.9 min (racemic).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 – 7.93 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 – 7.42 (m, 2H), 7.20 – 7.14 (m, 2H), 7.13 – 7.07 (m, 1H), 7.01 – 6.96 (m, 2H), 3.88 (q, *J* = 7.6 Hz, 1H), 2.70 – 2.60 (m, 1H), 2.56 – 2.48 (m, 1H), 2.42 – 2.33 (m, 1H), 2.25 – 2.13 (m, 1H), 1.95 – 1.83 (m, 2H), 1.74 – 1.61 (m, 1H), 1.61 – 1.50 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.7, 141.2, 138.0, 132.8, 128.8, 128.6, 128.1, 125.7, 49.6, 45.7, 36.7, 31.2, 27.9, 23.4.

FT-IR(film) 3025, 2954, 1681, 1652, 1447, 1224, 1002, 734, 699 cm^{-1}.

MS (ESI) m/z ([M+H]$^+$) calcd for $C_{19}H_{21}O$: 265.1587, found 265.1586.

The characterization data of this compound are consistent with a previous report.[5]

***n*-Bu$_3$SnH-mediated reductive cyclization (eq 5).** In a nitrogen-filled glovebox, *n*-Bu_3SnH (32 mg, 0.11 mmol) was added to DME (8.0 mL) in a 20 mL vial equipped with a stir bar and fitted with a PTFE septum cap. This mixture was stirred until it was homogeneous, and then the vial was removed from the glovebox and cooled to −60 °C. Next, 2-bromo-1-phenylhept-6-en-one (27 mg, 0.10 mmol) in DME (2.0 mL) was added via syringe, followed by BEt_3 (1.5 μL, 0.010 mmol) and air (0.2 mL). The resulting colorless solution was stirred at −60 °C for 20 h, and then the reaction was quenched with ethanol (1.0 mL). The resulting mixture was filtered through a bed of silica gel (height: 3.0 cm). The silica was washed with Et_2O (3 mL × 3), and then the combined filtrates were concentrated and dried under vacuum. The resulting residue was subjected to ^{1}H NMR analysis. The trans:cis ratio was found to be 1.4:1.

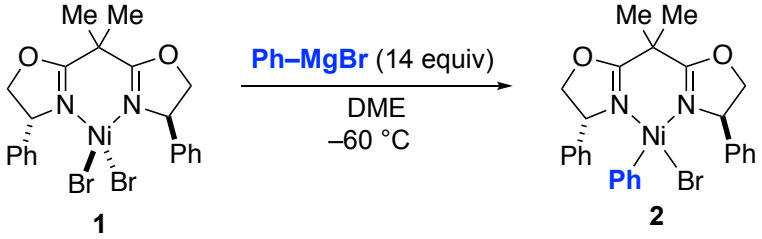
Dependence of U/C ratio on catalyst loading (Figure 14):

Table S–1. Ratio of uncyclized product (**U**) to cyclized (**C**) products.

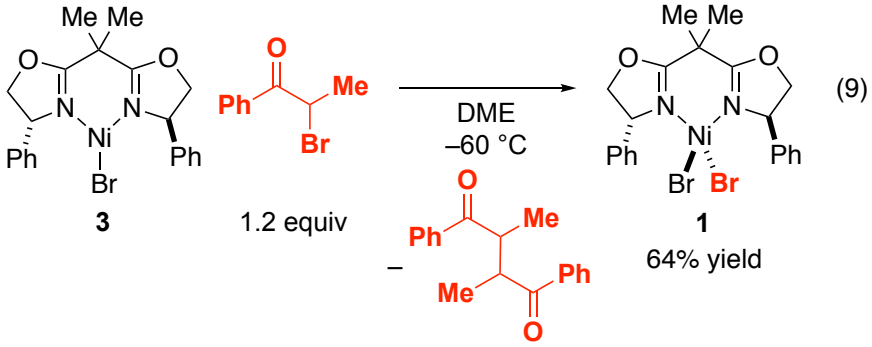
Ni loading / mol%	U/C*
2.0	0.45
4.0	0.82
6.0	1.28
8.0	1.67
10.0	2.27

* The **U**/**C** ratio was determined via ^{1}H NMR spectroscopy.

V. Stoichiometric Reactions



Transmetalation between $Ni^{II}Br_2$(Ph-BOX) and PhMgBr (Figure 12). In a nitrogen-filled glovebox, a solution of PhMgBr in Et_2O (3.0 M; 15 μL, 0.044 mmol) was added to DME (3.2 mL) in a quartz cuvette. The cuvette was then sealed with a puncturable screw cap and cooled to –60 °C, and a solution of ((*R*,*R*)-Ph-BOX)$Ni^{II}Br_2$ (1.5 mg, 0.0028 mmol) in DME (0.8 mL) was added via syringe over 10 s, with stirring. The reaction was monitored via UV-vis spectroscopy.



Abstraction by $Ni^{I}Br$(Ph-BOX) (3) of a halogen atom from the α-bromoketone (eq 9). In a nitrogen-filled glovebox, a 20 mL vial that contained $Ni^{I}Br$(Ph-BOX) (24 mg, 0.050 mmol; yellow solid) was cooled to –60 °C, and then a solution of DME (10 mL; pre-cooled to −60 °C) was added to the $Ni^{II}PhBr$(Ph-BOX). Then, with stirring, a solution that contained (±)-2-bromopropiophenone (9.0 μL, 0.060 mmol) in DME (0.20 mL) was added, resulting in an immediate color change to magenta. After 2 h of stirring at −60 °C, $Ni^{II}Br_2$(Ph-BOX) (**1**) was isolated by recrystallization from DME/*n*-pentane (64% yield). The supernatant was filtered through a short plug of silica gel, the volatiles were removed, and the residue was analyzed via ^{1}H NMR spectroscopy. The organic products were found to be primarily radical homo-coupling product (23% yield) and hydrodehalogenation product (10% yield).

Monitoring the reaction of $Ni^{I}Br$(Ph-BOX) (3) with the α-bromoketone or with PhMgBr via UV-vis spectroscopy. In a nitrogen-filled glovebox, $Ni^{I}Br$(Ph-BOX) (0.00068 mmol) was added to a cuvette equipped with a stir bar and fitted with a septum cap. The cuvette was removed from the glovebox and cooled to −60 °C. Pre-

cooled DME (3.8 mL; −60 °C) was added via syringe, which led to a homogeneous yellow solution. With stirring, a solution that contained (±)-2-bromopropiophenone (0.00082 mmol) or PhMgBr (3.0 M; 0.00082 mmol) in DME (0.2 mL) was added via syringe. The consumption of $Ni^{I}Br$(Ph-BOX) was monitored via UV-vis spectroscopy, at intervals of 6 s, by the disappearance of the absorption feature at 410 nm.

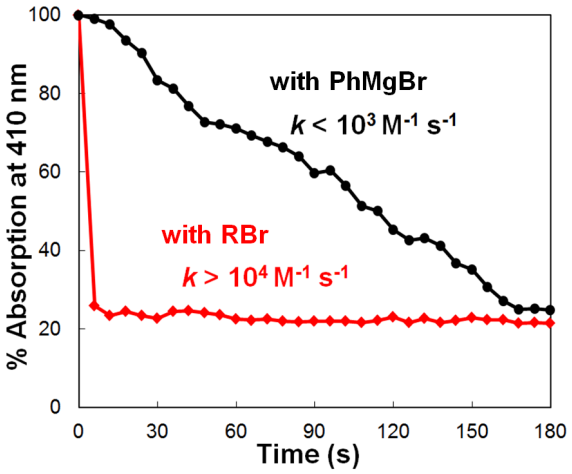
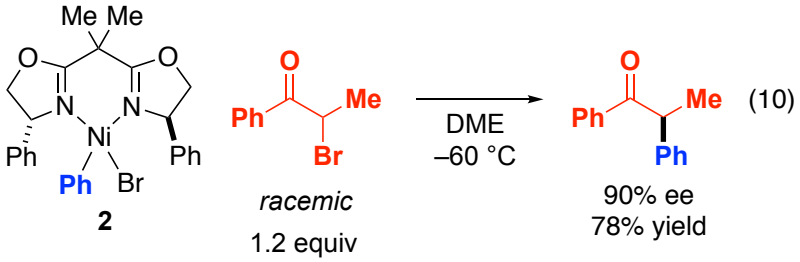


Figure S–3. Monitoring via UV-vis spectroscopy of the consumption of $Ni^{I}Br$(Ph-BOX) upon treatment with (±)-2-bromopropiophenone or PhMgBr.



Coupling of the resting state of nickel ($Ni^{II}PhBr$ (Ph-BOX), 2) with the α-bromoketone (eq 10; Figure 13). In a nitrogen-filled glovebox, a 40 mL vial that contained $Ni^{II}PhBr$(Ph-BOX) (7.8 mg, 0.014 mmol; orange solid) was cooled to −60 °C. Pre-cooled DME (20 mL; –60 °C) was added to the $Ni^{II}PhBr$(Ph-BOX). Then, with stirring, a solution of (±)-2-bromopropiophenone (3.6 mg, 0.017 mmol) in DME (0.20 mL) was added dropwise to the solution of $Ni^{II}PhBr$(Ph-BOX) in DME at −60 °C. After 6 h of stirring at −60 °C, the reaction was quenched by the addition of ethanol (0.2 mL). The reaction mixture was filtered through a short plug of silica gel and analyzed via GC and chiral HPLC. Calibrated GC yield: 78% (90% ee).

VI. EPR Data

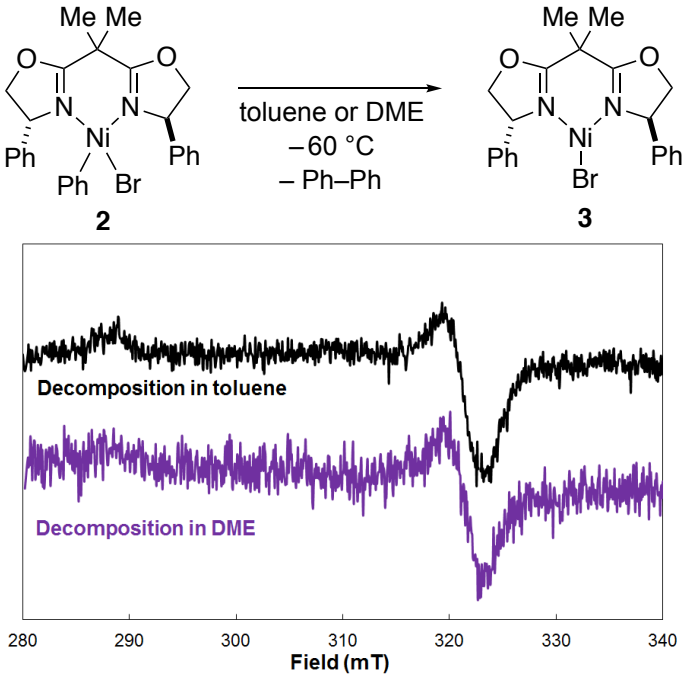


Figure S–4. Stability of Ni^{II}PhBr(Ph-BOX) (**2**) at −60 °C after 3 h in toluene (black trace) and in DME (purple trace): X-band EPR spectra. Quantification indicated that the quantity of Ni^{I}Br(Ph-BOX) (**3**) was <0.5% in both solvents. The spectra were collected at ν = 9.4 GHz, 2 mW power, and a modulation amplitude of 2 G.

VII. UV-Vis Data

General procedure for measuring UV-vis spectra of temperature-sensitive complexes. In a nitrogen-filled glovebox, the compound was added to a cuvette equipped with a stir bar and fitted with septum cap. The cuvette was removed from the glovebox and cooled to −60 °C. In a nitrogen-filled glovebox, DME was added to a 20 mL vial fitted with a PTFE septum cap. The vial was removed from the glovebox, and the solvent was frozen using liquid nitrogen. Upon melting, the cold DME (4 mL) was transferred quickly via syringe into the cuvette (equipped with a balloon) at –60 °C. The solution was stirred at −60 °C for ~15 s before collecting a spectrum.

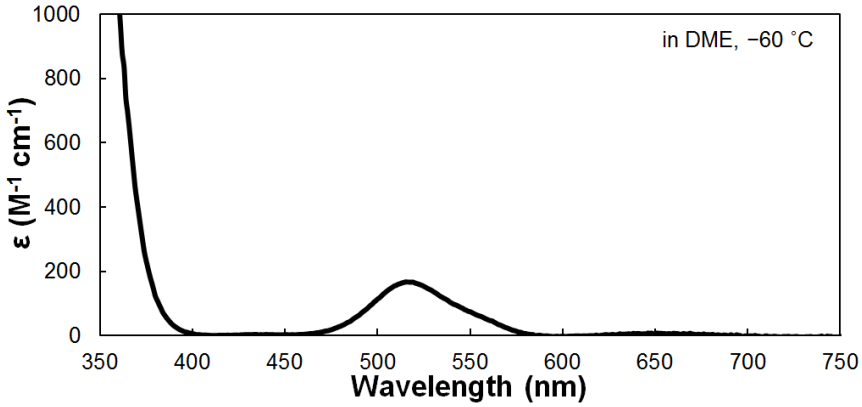


Figure S–5. UV-vis spectrum (DME, −60 °C) of ((*R*,*R*)-Ph-BOX)Ni^{II}Br$_2$ (**1**).

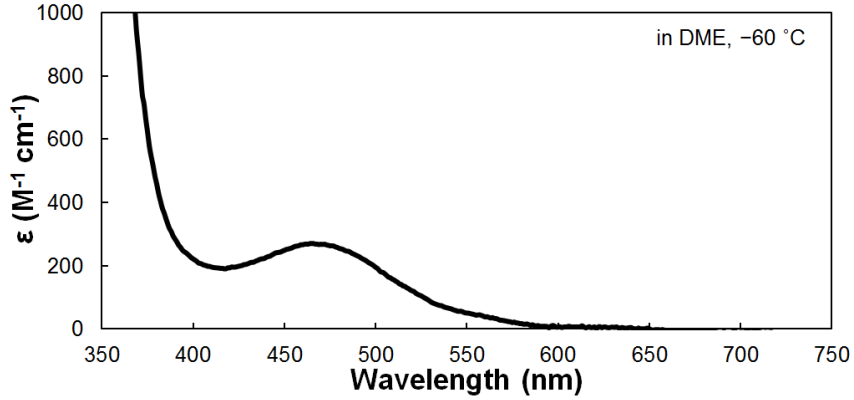


Figure S–6. UV-vis spectrum (DME, −60 °C) of ((*R*,*R*)-Ph-BOX)Ni^{II}PhBr (**2**).

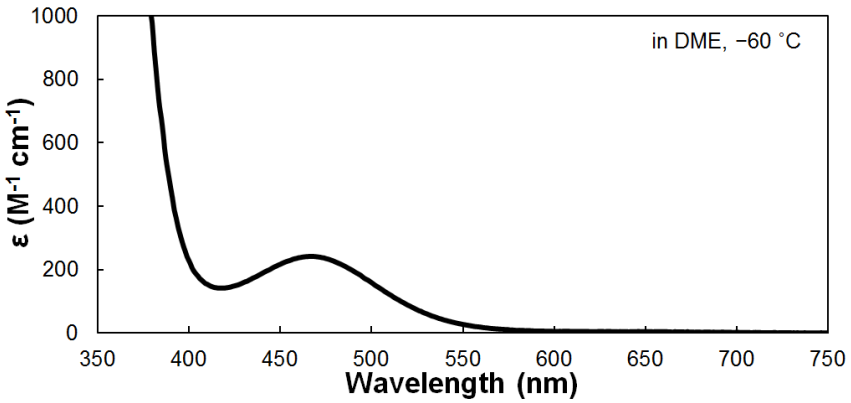


Figure S–7. UV-vis spectrum (DME, −60 °C) of ((*R*,*R*)-Ph-BOX^{Ph})Ni^{II}PhBr (**2^{Ph}**).

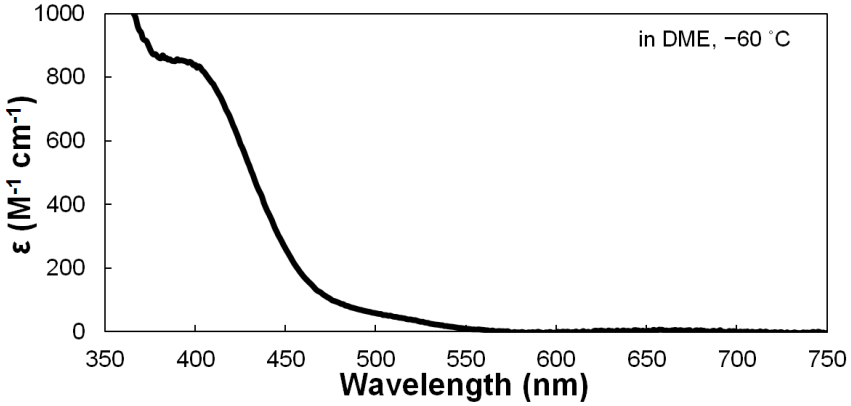
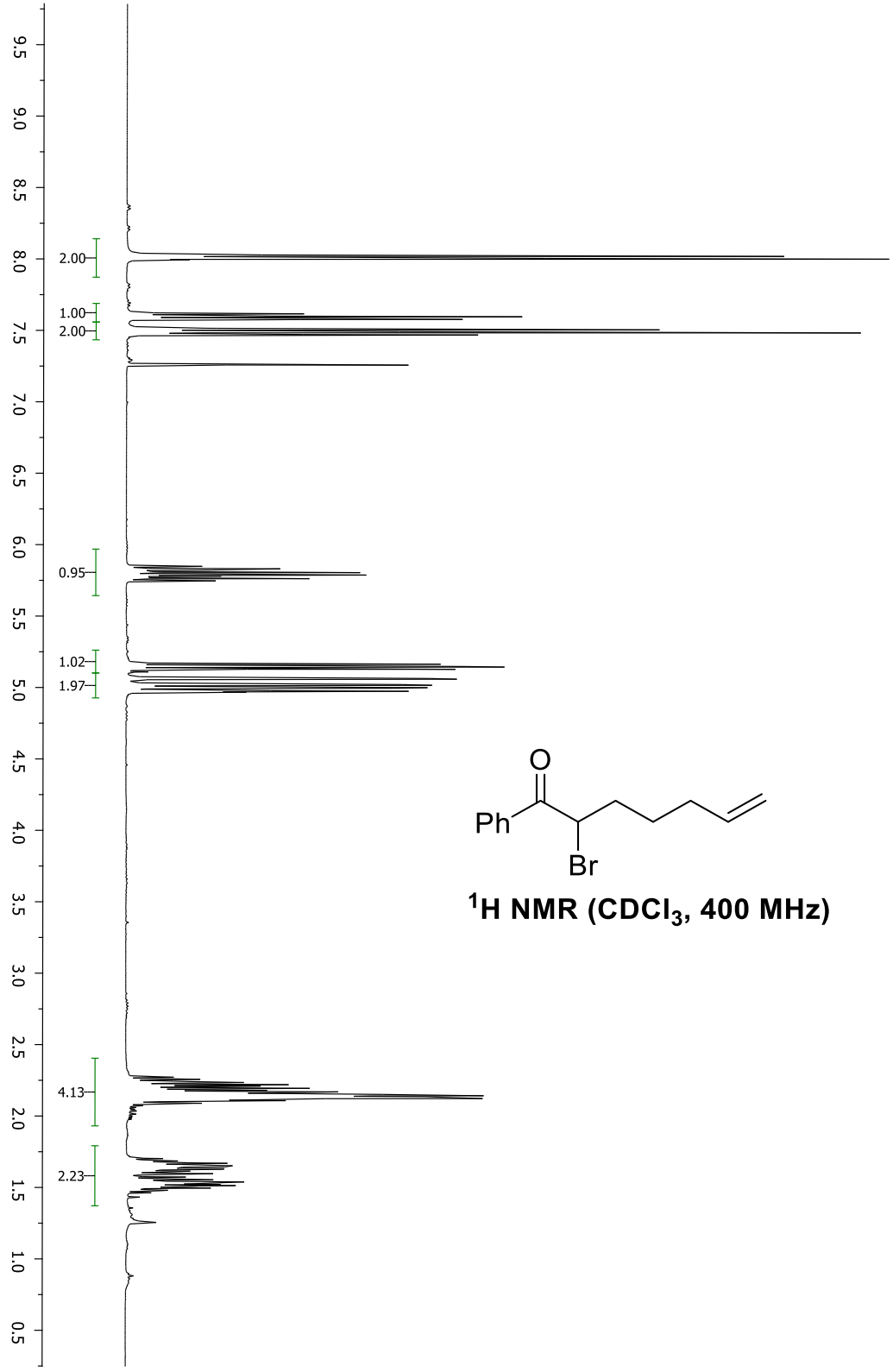
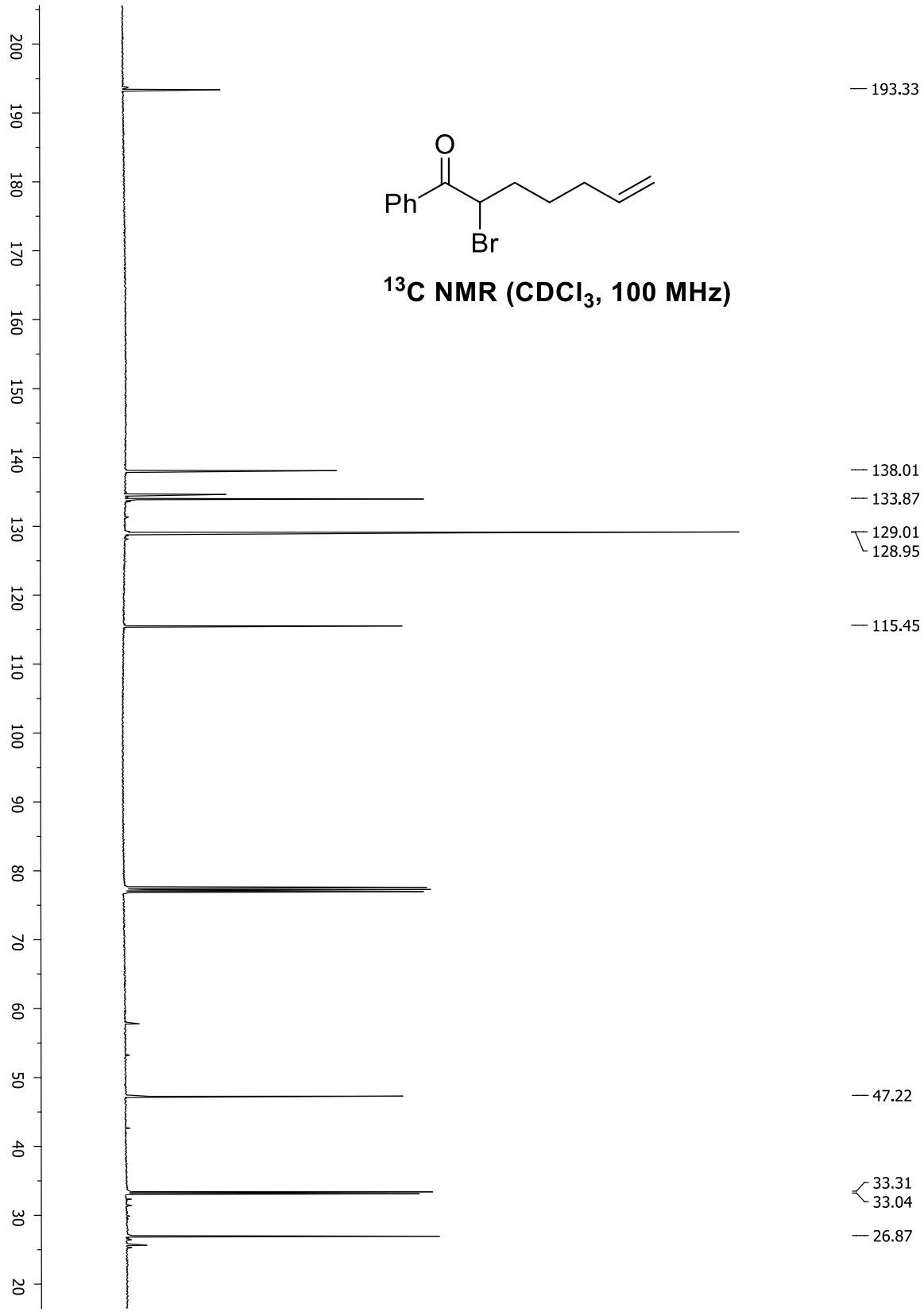


Figure S–8. UV-vis spectrum (DME, −60 °C) of ((*R*,*R*)-Ph-BOX)Ni^{I}Br (**3**).

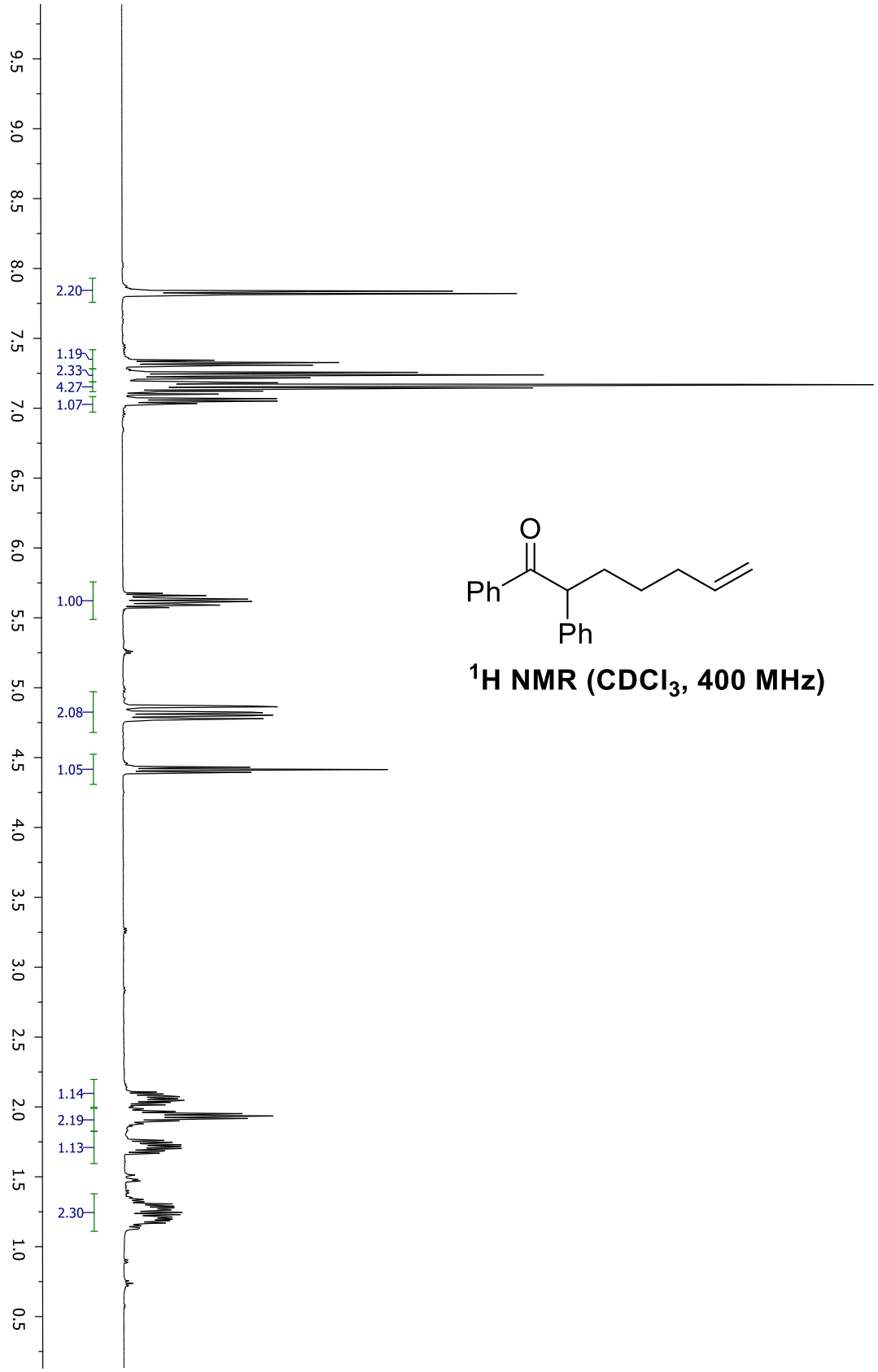
VIII. NMR Data

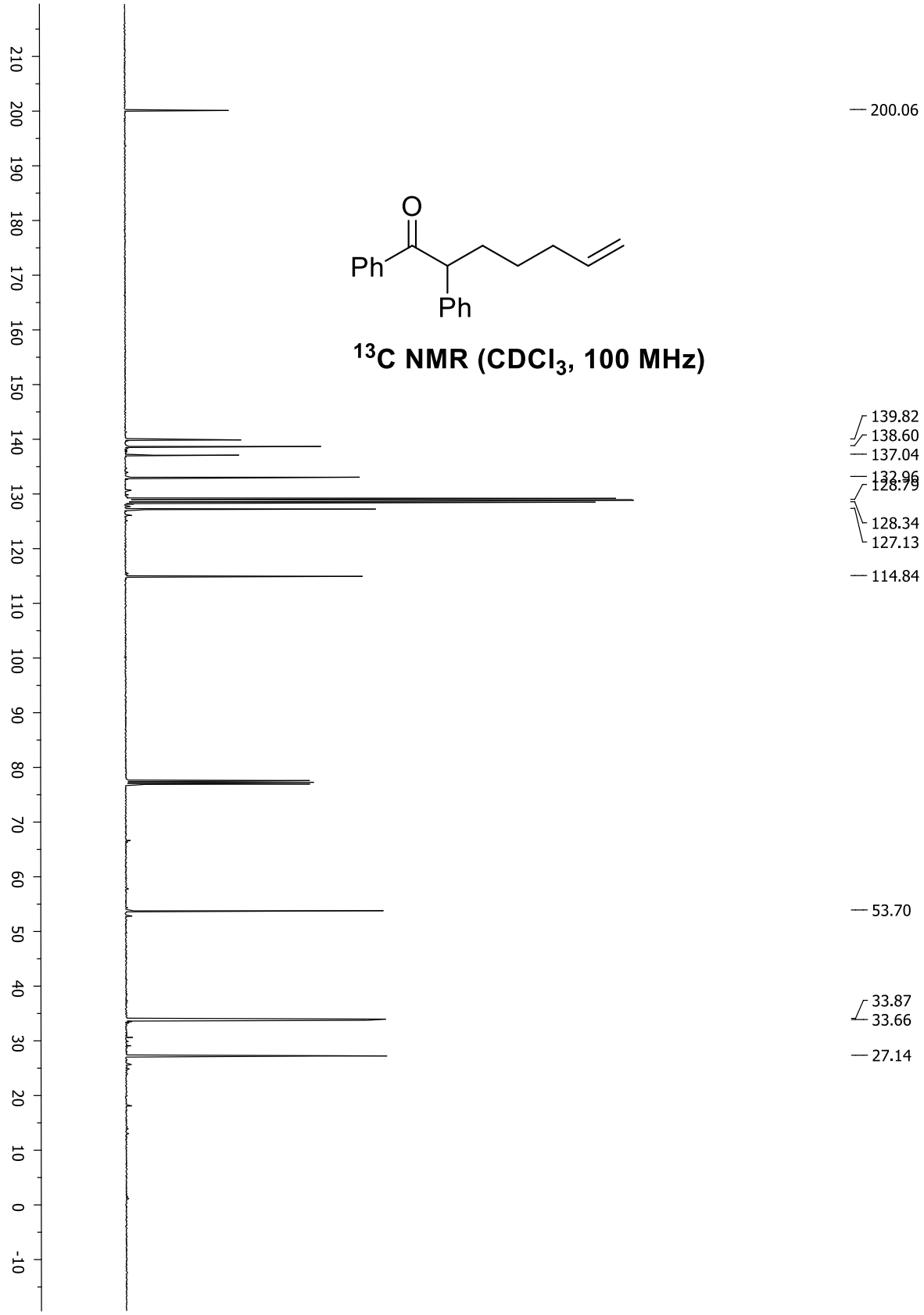


^{1}H NMR ($CDCl_3$, 400 MHz)

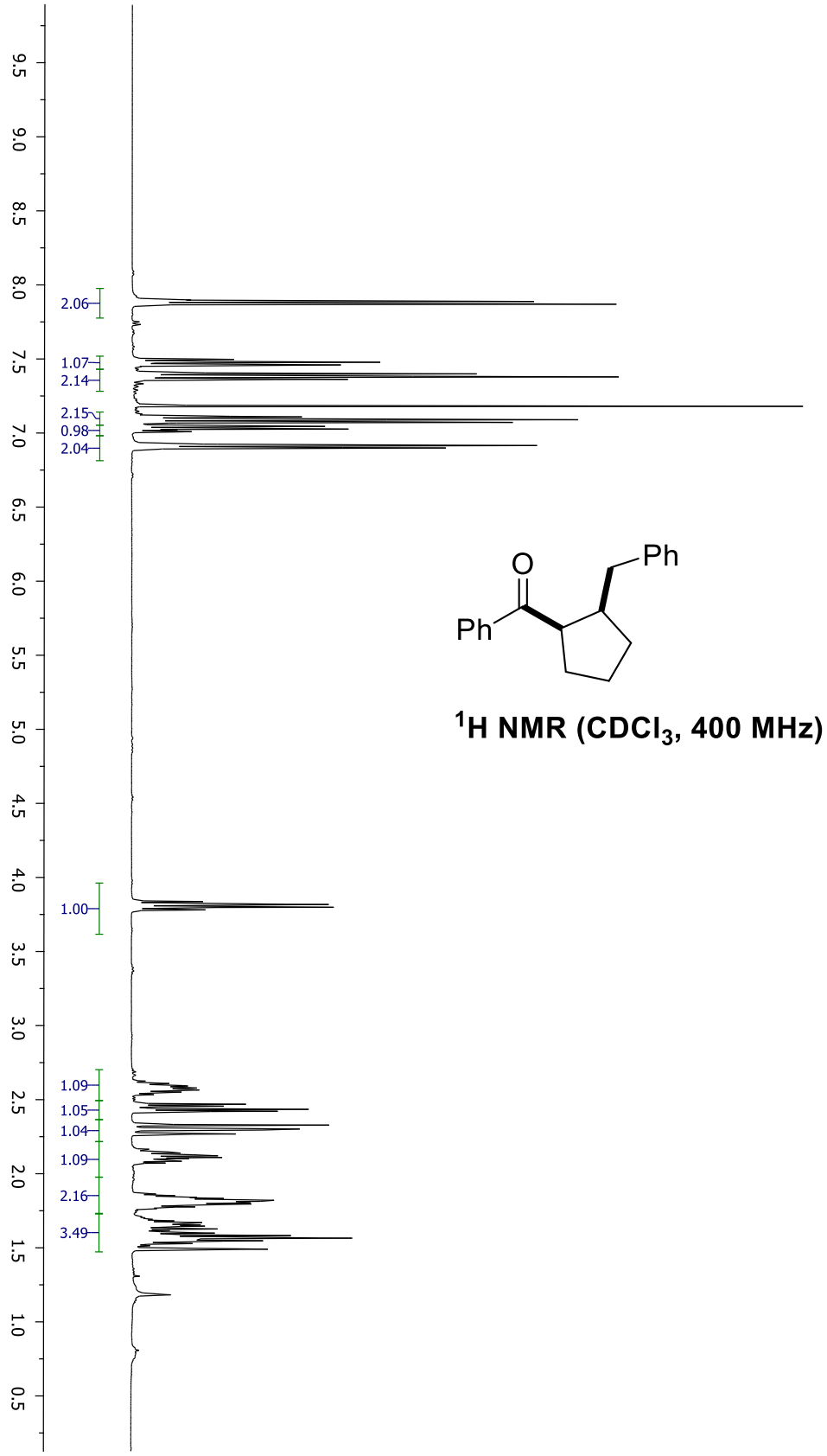


^{13}C NMR ($CDCl_3$, 100 MHz)

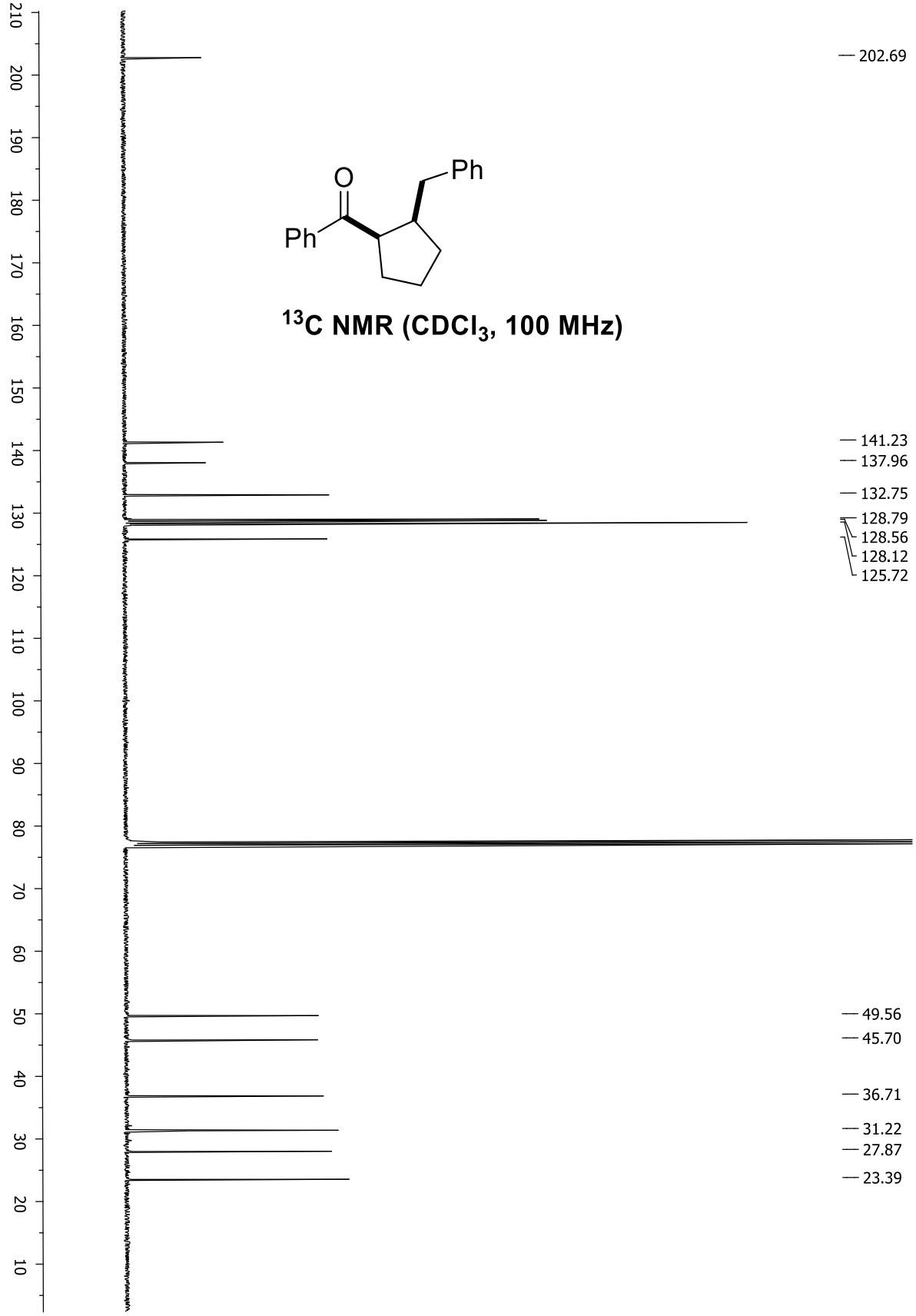

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2.20
1.19
2.33
4.27
1.07
1.00
2.08
1.05
1.14
2.19
1.13
2.30
O
Ph
Ph
^{1}H NMR (CDCl$_3$, 400 MHz)



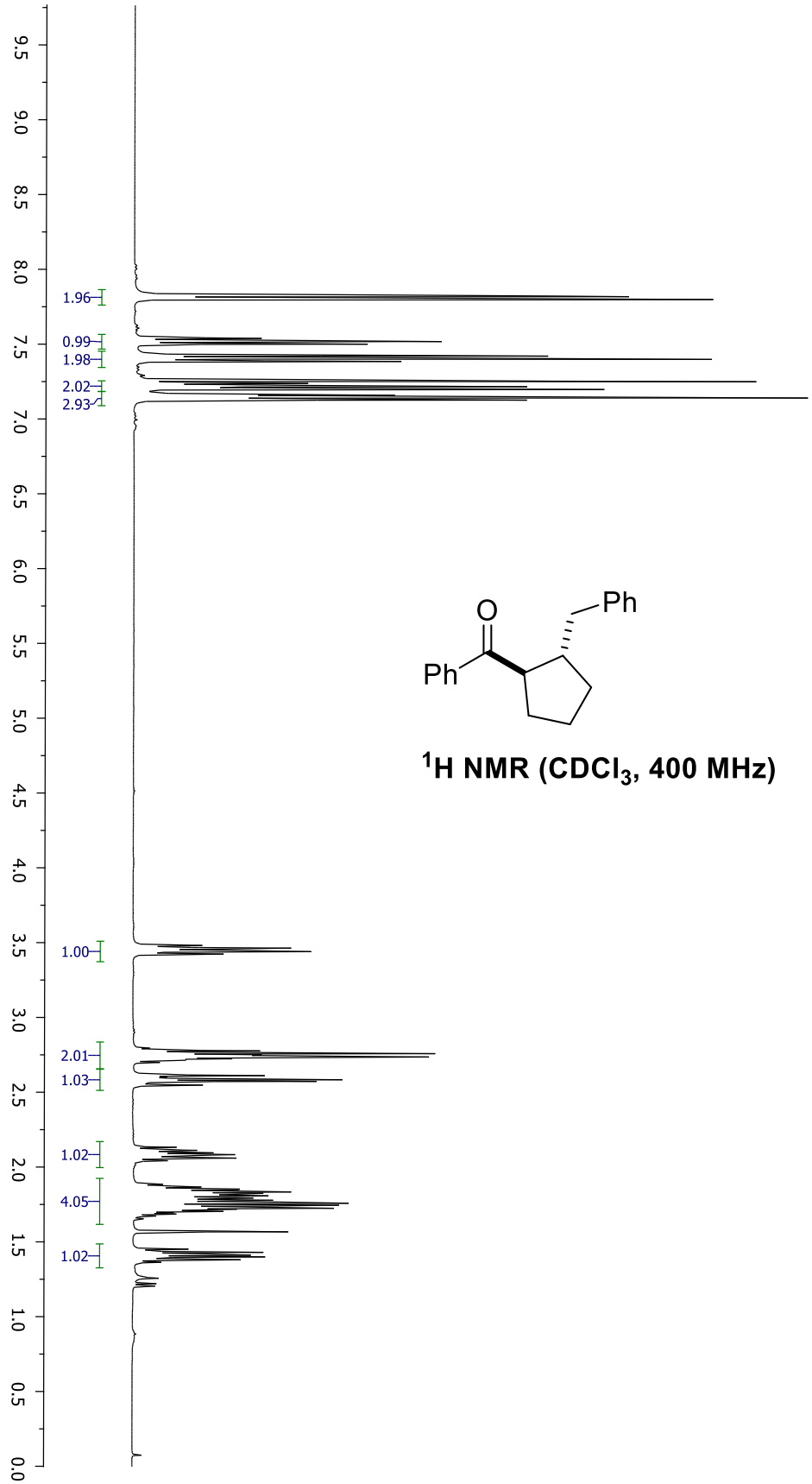
^{13}C NMR ($CDCl_3$, 100 MHz)



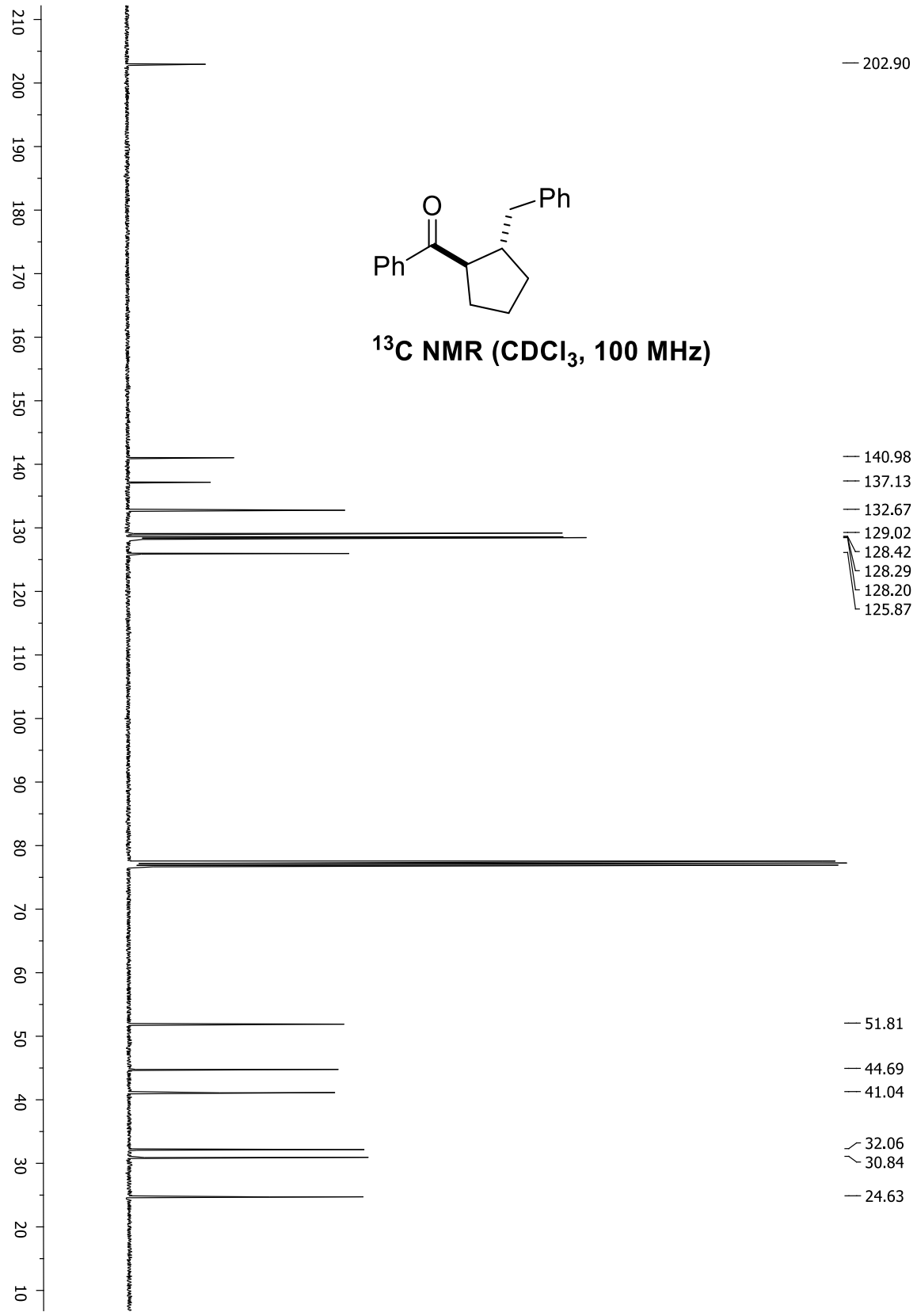
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 100 MHz)



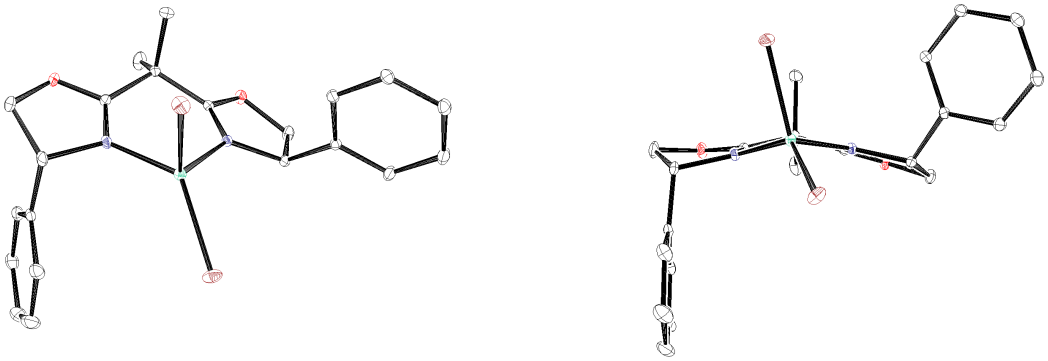
^{1}H NMR ($CDCl_3$, 400 MHz)


O
Ph
Ph
13C NMR (CDCl3, 100 MHz)
202.90
140.98
137.13
132.67
129.02
128.42
128.29
128.20
125.87
51.81
44.69
41.04
32.06
30.84
24.63

IX. X-Ray Crystallographic Data

General Procedure. A suitable crystal was selected and mounted in a nylon loop. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Mo−Kα radiation at a temperature of 100 K. Using Olex 2,[6] the structure was solved with the XT[7] structure solution program using Direct Methods and refined with the ShelXL[8] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter as well as the known stereochemistry of the ligand.

Side view **Front view**



ORTEP plots (side and front views) of $Ni^{II}Br_2$(Ph-BOX) (**1**), with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table S–2. Crystal data and structure refinement for $Ni^{II}Br_2$(Ph-BOX).

Identification code	((*R*,*R*)-Ph-BOX)$Ni^{II}Br_2$
Empirical formula	$C_{21}H_{22}Br_2N_2NiO_2$
Formula weight	552.94
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.9454(9)
b/Å	11.7746(13)
c/Å	20.350(3)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2143.4(4)
Z	4
ϱ_{calc}g/cm^3	1.713
μ/mm^{-1}	4.652
F(000)	1104.0
Crystal size/mm^3	0.24 × 0.22 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.3 to 72.72
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -33 ≤ l ≤ 33
Reflections collected	126446
Independent reflections	10383 [R_{int} = 0.0384, R_{sigma} = 0.0227]
Data/restraints/parameters	10383/0/256
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0184, wR_2 = 0.0419
Final R indexes [all data]	R_1 = 0.0214, wR_2 = 0.0425
Largest diff. peak/hole / e Å^{-3}	0.39/-0.90
Flack parameter	0.000(3)

Table S–3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ni^{II}Br_2$(Ph-BOX). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br(1)	2548.12(13)	1500.98(9)	6369.74(6)	21.18(2)
Br(2)	6135.42(11)	3425.55(10)	6016.47(6)	22.16(2)
Ni(1)	3598.53(13)	3347.18(10)	6288.33(6)	12.47(2)
O(1)	-450.5(9)	4842.0(8)	5834.1(4)	21.13(16)
O(2)	2208.0(9)	5477.3(7)	7779.3(4)	16.02(13)
N(1)	1846.1(10)	4095.5(7)	5880.3(4)	13.41(14)
N(2)	3296.1(9)	4227.8(7)	7105.8(4)	11.26(13)
C(1)	1444.1(13)	4080.5(10)	5163.3(5)	17.45(18)
C(2)	-239.6(14)	4296.5(13)	5193.1(6)	26.0(2)
C(3)	759.1(10)	4565.2(8)	6186.8(5)	13.79(16)
C(4)	630.8(11)	4807.1(9)	6914.3(5)	13.84(16)
C(5)	-303.1(13)	3836.7(12)	7220.4(6)	26.0(2)
C(6)	-150.3(14)	5954.7(12)	7020.1(7)	25.9(2)
C(7)	2132.5(10)	4816.4(8)	7250.2(5)	11.40(14)
C(8)	3740.4(12)	5398.7(9)	8028.0(5)	17.11(17)
C(9)	4459.4(11)	4451.9(8)	7609.7(5)	12.01(15)
C(10)	2363.5(12)	4977.0(9)	4819.0(5)	14.90(16)
C(11)	3737.5(14)	4687.2(11)	4542.1(6)	22.7(2)
C(12)	4647.5(15)	5520.0(13)	4264.2(7)	30.7(3)
C(13)	4186.1(15)	6640.2(13)	4262.9(7)	29.7(3)
C(14)	2815.8(15)	6936.3(11)	4531.2(6)	24.1(2)
C(15)	1909.5(12)	6108.4(10)	4806.8(5)	18.06(19)
C(16)	4863.7(9)	3407.5(8)	8002.7(5)	11.79(14)
C(17)	3930.1(11)	2464.2(8)	8050.6(5)	14.26(16)
C(18)	4308.1(11)	1564.0(9)	8461.1(5)	15.96(16)
C(19)	5611.9(12)	1598.1(10)	8831.7(5)	18.47(17)
C(20)	6551.7(13)	2535.6(11)	8781.4(6)	23.5(2)
C(21)	6187.5(11)	3432.8(10)	8366.1(6)	19.47(17)

Table S–4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Ni^{II}Br_2$(Ph-BOX). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	28.50(5)	12.19(4)	22.85(5)	-0.96(3)	0.04(4)	-2.29(4)
Br(2)	14.90(4)	24.04(5)	27.52(5)	-11.00(4)	5.78(4)	-2.35(4)
Ni(1)	13.88(5)	12.20(5)	11.32(5)	-2.64(4)	0.74(4)	1.18(4)
O(1)	12.5(3)	35.4(5)	15.4(3)	2.1(3)	-3.8(3)	-1.5(3)
O(2)	17.2(3)	17.9(3)	13.0(3)	-5.4(3)	-1.0(3)	4.0(3)
N(1)	16.5(3)	14.1(3)	9.7(3)	-0.4(3)	-1.5(3)	-1.7(3)
N(2)	12.0(3)	12.0(3)	9.8(3)	-0.4(3)	-0.3(2)	0.5(2)
C(1)	21.7(5)	20.1(4)	10.6(4)	-3.8(3)	-3.5(3)	-4.5(4)
C(2)	21.0(5)	41.2(7)	15.8(5)	-2.0(5)	-7.0(4)	-10.5(5)
C(3)	12.6(3)	15.5(4)	13.2(4)	0.9(3)	-2.0(3)	-2.1(3)
C(4)	11.1(3)	18.7(4)	11.7(4)	1.1(3)	0.6(3)	1.4(3)
C(5)	19.0(5)	39.7(7)	19.2(5)	8.1(5)	1.5(4)	-10.7(4)
C(6)	23.1(5)	31.6(6)	23.2(5)	-4.7(5)	-3.8(4)	15.4(5)
C(7)	13.6(3)	11.3(3)	9.3(3)	0.3(3)	1.0(3)	0.4(3)
C(8)	19.8(4)	15.5(4)	16.1(4)	-4.7(3)	-5.1(4)	2.4(3)
C(9)	12.1(3)	12.6(4)	11.3(4)	0.0(3)	-0.7(3)	-1.3(3)
C(10)	16.9(4)	19.3(4)	8.5(4)	-0.6(3)	-2.1(3)	0.7(3)
C(11)	23.2(5)	27.1(5)	17.8(5)	0.7(4)	2.8(4)	8.6(4)
C(12)	24.6(6)	41.6(7)	25.9(6)	5.1(5)	10.4(5)	5.7(5)
C(13)	29.2(6)	36.2(7)	23.6(6)	12.1(5)	3.8(4)	-3.2(5)
C(14)	29.5(6)	23.1(5)	19.6(5)	7.6(4)	-3.7(4)	2.5(4)
C(15)	18.4(4)	21.8(5)	14.0(4)	0.3(4)	-2.1(3)	4.6(4)
C(16)	11.5(3)	12.5(3)	11.3(4)	-0.1(3)	-0.1(3)	1.4(3)
C(17)	15.3(4)	14.3(4)	13.2(4)	1.0(3)	-1.0(3)	-1.4(3)
C(18)	19.9(4)	13.2(4)	14.7(4)	0.8(3)	0.0(3)	-0.2(3)
C(19)	20.4(4)	16.4(4)	18.6(4)	3.7(4)	-1.5(3)	5.0(4)
C(20)	18.6(4)	25.5(5)	26.4(6)	7.7(4)	-8.6(4)	0.0(4)
C(21)	14.1(4)	19.8(4)	24.5(5)	5.9(4)	-6.0(3)	-2.2(4)

Table S–5. Bond lengths /Å for $Ni^{II}Br_2$(Ph-BOX).

Br(1)	Ni(1)	2.3740(3)	C(4)	C(6)	1.5364(16)
Br(2)	Ni(1)	2.3376(3)	C(4)	C(7)	1.5073(13)
Ni(1)	N(1)	1.9808(9)	C(8)	C(9)	1.5431(14)
Ni(1)	N(2)	1.9788(8)	C(9)	C(16)	1.5108(13)
O(1)	C(2)	1.4663(16)	C(10)	C(11)	1.3944(16)
O(1)	C(3)	1.3387(12)	C(10)	C(15)	1.3930(16)
O(2)	C(7)	1.3303(12)	C(11)	C(12)	1.3944(19)
O(2)	C(8)	1.4641(13)	C(12)	C(13)	1.382(2)
N(1)	C(1)	1.5028(13)	C(13)	C(14)	1.3865(19)
N(1)	C(3)	1.2808(13)	C(14)	C(15)	1.3864(17)
N(2)	C(7)	1.2845(12)	C(16)	C(17)	1.3931(13)
N(2)	C(9)	1.4846(12)	C(16)	C(21)	1.3965(13)
C(1)	C(2)	1.5286(17)	C(17)	C(18)	1.3913(14)
C(1)	C(10)	1.5105(15)	C(18)	C(19)	1.3895(14)
C(3)	C(4)	1.5120(14)	C(19)	C(20)	1.3914(17)
C(4)	C(5)	1.5464(16)	C(20)	C(21)	1.3916(16)

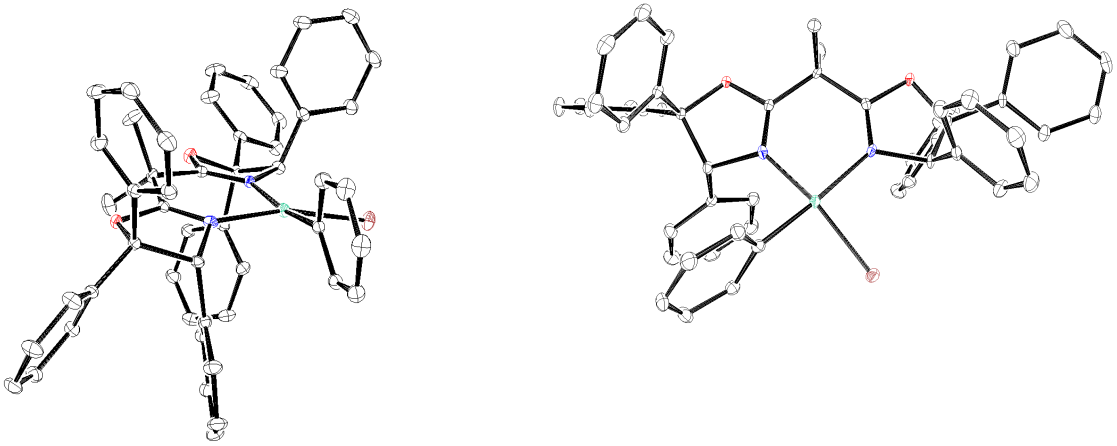
Table S–6. Bond angles /° for $Ni^{II}Br_2$(Ph-BOX).

Br(2)	Ni(1)	Br(1)	115.907(7)	C(7)	C(4)	C(5)	107.71(8)
N(1)	Ni(1)	Br(1)	97.09(3)	C(7)	C(4)	C(6)	109.60(9)
N(1)	Ni(1)	Br(2)	130.66(3)	O(2)	C(7)	C(4)	114.62(8)
N(2)	Ni(1)	Br(1)	111.54(3)	N(2)	C(7)	O(2)	117.36(8)
N(2)	Ni(1)	Br(2)	108.12(2)	N(2)	C(7)	C(4)	127.92(9)
N(2)	Ni(1)	N(1)	90.64(3)	O(2)	C(8)	C(9)	104.20(8)
C(3)	O(1)	C(2)	105.45(9)	N(2)	C(9)	C(8)	102.55(8)
C(7)	O(2)	C(8)	106.88(7)	N(2)	C(9)	C(16)	112.88(8)
C(1)	N(1)	Ni(1)	126.24(7)	C(16)	C(9)	C(8)	113.32(8)
C(3)	N(1)	Ni(1)	126.07(7)	C(11)	C(10)	C(1)	119.76(10)
C(3)	N(1)	C(1)	107.23(9)	C(15)	C(10)	C(1)	121.19(10)
C(7)	N(2)	Ni(1)	125.86(7)	C(15)	C(10)	C(11)	118.93(10)
C(7)	N(2)	C(9)	108.31(8)	C(12)	C(11)	C(10)	120.43(11)
C(9)	N(2)	Ni(1)	125.31(6)	C(13)	C(12)	C(11)	119.84(11)
N(1)	C(1)	C(2)	101.27(9)	C(12)	C(13)	C(14)	120.22(12)
N(1)	C(1)	C(10)	108.17(8)	C(15)	C(14)	C(13)	119.97(12)
C(10)	C(1)	C(2)	116.02(10)	C(14)	C(15)	C(10)	120.61(11)
O(1)	C(2)	C(1)	103.58(8)	C(17)	C(16)	C(9)	122.86(8)
O(1)	C(3)	C(4)	114.69(8)	C(17)	C(16)	C(21)	119.23(9)
N(1)	C(3)	O(1)	117.23(9)	C(21)	C(16)	C(9)	117.77(9)
N(1)	C(3)	C(4)	128.01(9)	C(18)	C(17)	C(16)	120.25(9)
C(3)	C(4)	C(5)	107.23(9)	C(19)	C(18)	C(17)	120.52(10)
C(3)	C(4)	C(6)	109.72(9)	C(18)	C(19)	C(20)	119.35(10)
C(6)	C(4)	C(5)	110.35(10)	C(19)	C(20)	C(21)	120.37(10)
C(7)	C(4)	C(3)	112.19(8)	C(20)	C(21)	C(16)	120.26(10)

Table S–7. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for $Ni^{II}Br_2$(Ph-BOX).

Atom	*x*	*y*	*z*	U(eq)
H(1)	1650	3315	4971	21
H(2A)	-563	4803	4832	31
H(2B)	-806	3575	5166	31
H(5A)	-1317	3853	7038	39
H(5B)	-349	3937	7698	39
H(5C)	165	3105	7119	39
H(6A)	517	6570	6882	39
H(6B)	-396	6045	7486	39
H(6C)	-1070	5981	6759	39
H(8A)	3748	5195	8500	21
H(8B)	4277	6127	7969	21
H(9)	5377	4755	7390	14
H(11)	4056	3917	4543	27
H(12)	5583	5318	4076	37
H(13)	4810	7209	4077	36
H(14)	2498	7706	4526	29
H(15)	970	6315	4989	22
H(17)	3032	2435	7802	17
H(18)	3670	921	8488	19
H(19)	5859	987	9117	22
H(20)	7447	2563	9032	28
H(21)	6842	4065	8330	23

Side view **Top view**



ORTEP plots (side and top views) of $Ni^{II}PhBr(Ph\text{-}BOX^{Ph})$ (**2**^{Ph}), with thermal ellipsoids at the 30% probability level. Interstitial THF molecule and hydrogen atoms have been omitted for clarity.

Table S–8. Crystal data and structure refinement for $Ni^{II}PhBr(Ph\text{-}BOX^{Ph})$.

Identification code	((*R*,*R*)-Ph-BOX^{Ph})$Ni^{II}PhBr$
Empirical formula	$C_{55}H_{51}BrN_2NiO_3$
Formula weight	926.60
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.7540(5)
b/Å	17.1117(16)
c/Å	26.830(3)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/$Å^3$	4478.2(7)
Z	4
$\rho_{calc}g/cm^3$	1.374
μ/mm^{-1}	2.036
F(000)	1928.0
Crystal size/mm^3	0.14 × 0.08 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.12 to 145.54
Index ranges	$-12 \le h \le 12$, $-21 \le k \le 15$, $-33 \le l \le 29$
Reflections collected	32200
Independent reflections	8614 [R_{int} = 0.0475, R_{sigma} = 0.0415]
Data/restraints/parameters	8614/0/562
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.1112
Final R indexes [all data]	R_1 = 0.0501, wR_2 = 0.1144
Largest diff. peak/hole / e $Å^{-3}$	1.55/-0.60
Flack parameter	0.00(2)

Table S–9. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ni^{II}PhBr(Ph\text{-}BOX^{Ph})$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br(1)	7939.4(4)	5185.3(2)	4145.79(17)	24.92(10)
Ni(1)	6269.1(6)	4236.2(3)	4073.1(2)	16.19(14)
O(1)	2735(3)	5212.5(14)	4693.0(9)	18.7(5)
O(2)	2885(3)	2915.7(13)	3709.6(9)	15.3(5)
N(1)	4807(3)	4850.7(18)	4410(1)	14.9(6)
N(2)	4900(3)	3521.3(17)	3836.5(11)	16.4(6)
C(1)	7684(4)	3549(2)	3853.6(14)	19.4(8)
C(2)	8274(4)	3573(2)	3383.0(14)	21.9(8)
C(3)	9178(4)	2982(3)	3232.7(16)	29.6(10)
C(4)	9518(5)	2387(2)	3563.7(17)	30.3(10)
C(5)	8987(4)	2382(2)	4029.9(18)	32.2(10)
C(6)	8047(4)	2957(2)	4176.0(15)	25.7(8)
C(7)	3546(4)	4681.0(19)	4461.2(13)	14.9(7)
C(8)	3541(4)	5948.0(19)	4665.8(13)	16.4(7)
C(9)	5011(4)	5618(2)	4674.3(13)	16.1(7)
C(10)	5595(4)	5484(2)	5190.9(14)	19.5(8)
C(11)	5199(4)	4868(3)	5495.0(14)	25.7(8)
C(12)	5727(5)	4798(3)	5971.0(15)	30.7(9)
C(13)	6677(5)	5328(3)	6147.9(16)	32.8(10)
C(14)	7074(5)	5947(3)	5847.5(16)	33.6(9)
C(15)	6552(4)	6026(2)	5373.8(16)	27.4(9)
C(16)	3129(4)	6312.4(19)	4165.7(14)	18.8(7)
C(17)	3925(4)	6248(2)	3740.1(14)	23.1(8)
C(18)	3437(5)	6524(3)	3288.8(16)	29.0(9)
C(19)	2147(5)	6858(3)	3255.9(16)	32.7(9)
C(20)	1356(4)	6937(3)	3683.9(15)	29.8(9)
C(21)	1838(4)	6661(2)	4132.3(16)	26.6(8)
C(22)	3156(4)	6466(2)	5101.6(13)	17.8(7)
C(23)	3722(4)	7218(2)	5123.3(15)	24.6(8)
C(24)	3354(4)	7724(2)	5499.4(16)	27.5(9)
C(25)	2429(4)	7493(2)	5861.3(17)	32.1(10)
C(26)	1899(5)	6749(3)	5849.0(17)	36.5(10)
C(27)	2266(5)	6234(2)	5471.0(15)	29.4(9)
C(28)	2777(4)	3962(2)	4294.6(13)	17.5(7)

C(29)	1449(4)	4220(3)	4031.5(18)	34.8(10)
C(30)	2433(5)	3454(3)	4758.3(16)	35.4(11)
C(31)	3618(4)	3478(2)	3944.6(12)	14.0(7)
C(32)	3892(4)	2401(2)	3465.8(13)	15.0(7)
C(33)	5122(4)	2976(2)	3407.4(13)	15.9(7)
C(34)	5175(4)	3445(2)	2926.8(14)	17.9(7)
C(35)	4606(4)	4188(2)	2878.3(15)	23.8(8)
C(36)	4665(5)	4569(3)	2419.5(16)	30.8(10)
C(37)	5257(5)	4217(3)	2012.6(16)	30.6(9)
C(38)	5824(5)	3485(3)	2059.8(15)	31.3(10)
C(39)	5795(4)	3102(2)	2513.7(14)	25.7(9)
C(40)	3236(4)	2096(2)	2989.6(13)	17.8(7)
C(41)	2425(4)	2585(2)	2698.7(14)	19.8(8)
C(42)	1856(4)	2318(2)	2257.8(15)	24.6(8)
C(43)	2087(5)	1559(2)	2097.7(15)	27.5(8)
C(44)	2901(5)	1076(2)	2382.6(15)	30.5(9)
C(45)	3462(4)	1335(2)	2829.2(15)	25.0(9)
C(46)	4252(4)	1753(2)	3836.3(14)	17.9(7)
C(47)	5472(4)	1334(2)	3788.8(15)	22.1(8)
C(48)	5761(4)	715(2)	4107.8(17)	28.6(9)
C(49)	4849(5)	523(2)	4486.6(16)	30.0(9)
C(50)	3654(5)	937(2)	4542.4(15)	29.9(9)
C(51)	3339(4)	1550(2)	4212.2(15)	25.3(8)
O(00I)	3166(4)	4770(2)	6800.7(14)	55.3(10)
C(52)	3586(6)	5573(3)	6878(2)	48.2(13)
C(53)	4565(7)	5562(4)	7303(3)	62.7(17)
C(54)	4147(9)	4871(5)	7609(3)	88(2)
C(55)	3661(10)	4332(4)	7213(2)	84(3)

Table S–10. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Ni^{II}PhBr(Ph\text{-}BOX^{Ph})$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	20.31(17)	15.75(17)	38.7(2)	-4.21(17)	3.57(17)	-2.16(15)
Ni(1)	16.4(3)	13.4(3)	18.8(3)	-3.4(2)	-0.8(3)	0.2(2)
O(1)	21.1(13)	10.2(11)	24.8(13)	-5.5(11)	3.4(10)	-1.3(11)
O(2)	16.3(11)	12.4(11)	17.2(12)	-3.9(9)	1.3(10)	-1.4(10)
N(1)	19.1(14)	10.7(13)	14.7(14)	-2.1(12)	-1.9(11)	-2.8(12)
N(2)	21.0(16)	14.6(15)	13.5(15)	-2.8(12)	-0.1(12)	2.6(12)
C(1)	15.9(18)	22.3(18)	20.1(18)	-2.7(15)	-1.6(14)	-2.5(14)
C(2)	22.2(19)	22.3(19)	21.2(19)	-0.5(15)	-2.8(15)	-3.2(15)
C(3)	25(2)	38(2)	26(2)	-11.9(19)	5.2(17)	0.9(18)
C(4)	29(2)	20(2)	42(3)	-10.1(18)	3.7(19)	4.6(17)
C(5)	29(2)	23(2)	45(3)	0.3(18)	1(2)	3.0(17)
C(6)	26.1(19)	26.5(19)	24.5(19)	-3.1(17)	0.8(18)	1.0(16)
C(7)	18.5(17)	12.5(17)	13.7(16)	-1.9(13)	0.9(13)	2.7(13)
C(8)	22.9(18)	7.7(16)	18.6(17)	-2.5(13)	3.7(14)	-2.4(14)
C(9)	21.8(18)	8.8(16)	17.6(17)	-5.5(13)	-1.2(14)	1.2(13)
C(10)	21.1(18)	18.9(17)	18.4(19)	-7.1(15)	-0.8(15)	1.6(14)
C(11)	36(2)	22.8(19)	18.5(19)	0.1(17)	-1.1(16)	-0.6(18)
C(12)	42(2)	29(2)	21(2)	3.6(18)	-3.8(17)	-2.1(19)
C(13)	36(2)	41(3)	22(2)	-3.3(18)	-6.3(17)	4.5(19)
C(14)	34(2)	38(2)	29(2)	-11.2(19)	-8(2)	-5.5(19)
C(15)	32(2)	23(2)	27(2)	-2.0(16)	-5.2(17)	-6.5(17)
C(16)	23.1(18)	15.0(15)	18.2(17)	-1.3(15)	-2.7(16)	-0.5(13)
C(17)	24(2)	20.9(19)	24(2)	2.8(15)	2.5(16)	-0.1(16)
C(18)	35(2)	31(2)	20(2)	5.4(17)	4.2(17)	1.9(18)
C(19)	41(2)	34(2)	23(2)	5.5(17)	-5(2)	4(2)
C(20)	26(2)	37(2)	27(2)	1.5(18)	-5.3(17)	3.3(19)
C(21)	22.1(18)	35(2)	22.3(19)	0.0(18)	1.9(17)	2.3(16)
C(22)	25.0(19)	11.6(16)	16.9(17)	-5.9(14)	-3.1(15)	3.1(14)
C(23)	29(2)	15.8(18)	29(2)	-3.5(15)	-2.0(17)	2.0(16)
C(24)	28(2)	19.7(19)	35(2)	-9.3(17)	-8.1(17)	6.3(15)
C(25)	45(2)	28(2)	23.4(19)	-10.9(19)	-3.6(19)	15.5(18)
C(26)	53(3)	33(2)	23(2)	-0.1(19)	12(2)	6(2)
C(27)	46(3)	19.0(18)	23(2)	-0.8(16)	7.4(19)	1.8(18)
C(28)	20.8(18)	12.1(15)	19.8(17)	-5.5(13)	3.0(14)	-7.3(14)
C(29)	26(2)	30(2)	48(3)	-19(2)	-6.0(19)	2.2(17)

C(30)	57(3)	23(2)	26(2)	-5.0(18)	22(2)	-14(2)
C(31)	17.2(17)	11.7(15)	13.1(16)	-0.8(13)	-2.4(13)	-0.8(14)
C(32)	17.6(17)	11.9(16)	15.4(16)	-2.9(13)	1.3(14)	-1.4(14)
C(33)	20.3(17)	14.8(17)	12.5(17)	-3.4(14)	-0.5(14)	-1.0(14)
C(34)	19.5(18)	14.3(17)	20.0(19)	-0.8(14)	0.3(14)	-3.5(14)
C(35)	29(2)	18.2(19)	24(2)	2.5(16)	0.2(16)	-0.6(16)
C(36)	40(3)	24(2)	28(2)	3.8(17)	-0.8(19)	-3.4(18)
C(37)	37(2)	31(2)	24(2)	9.9(18)	2.0(18)	-9.6(19)
C(38)	41(3)	37(2)	15.8(19)	1.8(17)	5.5(18)	-4(2)
C(39)	34(2)	24(2)	19(2)	-2.2(16)	3.8(16)	-0.3(17)
C(40)	20.6(19)	18.1(18)	14.8(17)	-1.9(14)	-0.9(14)	-3.1(14)
C(41)	22.4(19)	15.6(17)	21.3(18)	-3.6(15)	-0.6(14)	1.9(14)
C(42)	27(2)	23.5(19)	23.5(19)	3.8(16)	-5.3(16)	0.5(16)
C(43)	36(2)	28(2)	18.5(18)	-4.6(16)	-6.5(18)	-2(2)
C(44)	47(3)	21.7(19)	23(2)	-10.2(16)	-6(2)	1(2)
C(45)	34(2)	17.2(18)	24(2)	-2.5(15)	-6.9(17)	4.6(16)
C(46)	23.6(18)	13.0(17)	17.0(18)	-2.2(14)	-3.8(15)	-2.6(14)
C(47)	26(2)	20.7(19)	19.9(19)	-4.0(16)	-1.3(15)	-1.3(15)
C(48)	32(2)	21.1(18)	33(2)	0.2(19)	-8.9(19)	4.7(16)
C(49)	40(2)	23(2)	27(2)	4.8(17)	-11.3(19)	-5.5(18)
C(50)	46(3)	23(2)	20.9(19)	4.7(16)	0.5(19)	-6.8(19)
C(51)	31(2)	17.5(17)	27(2)	-0.2(16)	1.3(16)	-3.5(15)
O(00I)	75(3)	49(2)	41(2)	-13.2(18)	5.1(19)	-7(2)
C(52)	54(3)	36(3)	55(3)	-3(2)	5(3)	4(3)
C(53)	60(4)	60(4)	68(4)	-20(3)	-7(3)	-2(3)
C(54)	98(6)	93(6)	72(5)	-9(5)	-16(4)	30(5)
C(55)	157(8)	47(4)	49(4)	5(3)	15(4)	23(5)

Table S–11. Bond lengths for $Ni^{II}PhBr(Ph\text{-}BOX^{Ph})$.

Br(1)	Ni(1)	2.3087(7)	C(22)	C(27)	1.376(6)
Ni(1)	N(1)	1.989(3)	C(23)	C(24)	1.378(6)
Ni(1)	N(2)	1.919(3)	C(24)	C(25)	1.383(6)
Ni(1)	C(1)	1.906(4)	C(25)	C(26)	1.375(6)
O(1)	C(7)	1.356(4)	C(26)	C(27)	1.391(6)
O(1)	C(8)	1.486(4)	C(28)	C(29)	1.540(6)
O(2)	C(31)	1.354(4)	C(28)	C(30)	1.554(5)
O(2)	C(32)	1.472(4)	C(28)	C(31)	1.497(5)
N(1)	C(7)	1.271(5)	C(32)	C(33)	1.559(5)
N(1)	C(9)	1.506(4)	C(32)	C(40)	1.521(5)
N(2)	C(31)	1.286(5)	C(32)	C(46)	1.531(5)
N(2)	C(33)	1.497(4)	C(33)	C(34)	1.519(5)
C(1)	C(2)	1.388(5)	C(34)	C(35)	1.394(5)
C(1)	C(6)	1.379(6)	C(34)	C(39)	1.393(5)
C(2)	C(3)	1.400(6)	C(35)	C(36)	1.394(6)
C(3)	C(4)	1.391(7)	C(36)	C(37)	1.374(6)
C(4)	C(5)	1.354(7)	C(37)	C(38)	1.374(6)
C(5)	C(6)	1.400(6)	C(38)	C(39)	1.384(6)
C(7)	C(28)	1.509(5)	C(40)	C(41)	1.390(5)
C(8)	C(9)	1.541(5)	C(40)	C(45)	1.390(5)
C(8)	C(16)	1.533(5)	C(41)	C(42)	1.384(5)
C(8)	C(22)	1.515(5)	C(42)	C(43)	1.385(6)
C(9)	C(10)	1.516(5)	C(43)	C(44)	1.378(6)
C(10)	C(11)	1.388(6)	C(44)	C(45)	1.389(6)
C(10)	C(15)	1.404(5)	C(46)	C(47)	1.395(5)
C(11)	C(12)	1.382(6)	C(46)	C(51)	1.390(5)
C(12)	C(13)	1.381(6)	C(47)	C(48)	1.390(6)
C(13)	C(14)	1.387(7)	C(48)	C(49)	1.390(6)
C(14)	C(15)	1.376(6)	C(49)	C(50)	1.372(7)
C(16)	C(17)	1.385(5)	C(50)	C(51)	1.407(6)
C(16)	C(21)	1.397(5)	O(00I)	C(52)	1.449(6)
C(17)	C(18)	1.384(6)	O(00I)	C(55)	1.419(8)
C(18)	C(19)	1.384(6)	C(52)	C(53)	1.488(9)
C(19)	C(20)	1.390(6)	C(53)	C(54)	1.496(11)
C(20)	C(21)	1.375(6)	C(54)	C(55)	1.485(11)
C(22)	C(23)	1.401(5)			

Table S–12. Bond angles for $Ni^{II}PhBr(Ph\text{-}BOX^{Ph})$.

N(1)	Ni(1)	Br(1)	95.49(9)	C(24)	C(23)	C(22)	120.3(4)
N(2)	Ni(1)	Br(1)	165.34(10)	C(23)	C(24)	C(25)	120.3(4)
N(2)	Ni(1)	N(1)	89.33(12)	C(26)	C(25)	C(24)	119.5(4)
C(1)	Ni(1)	Br(1)	87.07(11)	C(25)	C(26)	C(27)	120.5(4)
C(1)	Ni(1)	N(1)	170.23(15)	C(22)	C(27)	C(26)	120.3(4)
C(1)	Ni(1)	N(2)	90.49(14)	C(7)	C(28)	C(29)	108.6(3)
C(7)	O(1)	C(8)	103.7(3)	C(7)	C(28)	C(30)	109.0(3)
C(31)	O(2)	C(32)	106.2(3)	C(29)	C(28)	C(30)	110.3(4)
C(7)	N(1)	Ni(1)	128.5(2)	C(31)	C(28)	C(7)	111.4(3)
C(7)	N(1)	C(9)	106.1(3)	C(31)	C(28)	C(29)	109.4(3)
C(9)	N(1)	Ni(1)	125.5(2)	C(31)	C(28)	C(30)	108.1(3)
C(31)	N(2)	Ni(1)	129.7(3)	O(2)	C(31)	C(28)	113.3(3)
C(31)	N(2)	C(33)	106.1(3)	N(2)	C(31)	O(2)	116.7(3)
C(33)	N(2)	Ni(1)	123.4(2)	N(2)	C(31)	C(28)	130.0(3)
C(2)	C(1)	Ni(1)	124.3(3)	O(2)	C(32)	C(33)	100.4(3)
C(6)	C(1)	Ni(1)	116.5(3)	O(2)	C(32)	C(40)	107.3(3)
C(6)	C(1)	C(2)	119.0(4)	O(2)	C(32)	C(46)	107.3(3)
C(1)	C(2)	C(3)	120.1(4)	C(40)	C(32)	C(33)	117.1(3)
C(4)	C(3)	C(2)	119.6(4)	C(40)	C(32)	C(46)	113.2(3)
C(5)	C(4)	C(3)	120.3(4)	C(46)	C(32)	C(33)	110.3(3)
C(4)	C(5)	C(6)	120.3(4)	N(2)	C(33)	C(32)	101.8(3)
C(1)	C(6)	C(5)	120.6(4)	N(2)	C(33)	C(34)	109.2(3)
O(1)	C(7)	C(28)	113.1(3)	C(34)	C(33)	C(32)	116.4(3)
N(1)	C(7)	O(1)	117.4(3)	C(35)	C(34)	C(33)	123.2(3)
N(1)	C(7)	C(28)	129.4(3)	C(39)	C(34)	C(33)	117.9(3)
O(1)	C(8)	C(9)	100.5(3)	C(39)	C(34)	C(35)	118.9(4)
O(1)	C(8)	C(16)	104.4(3)	C(34)	C(35)	C(36)	119.5(4)
O(1)	C(8)	C(22)	109.1(3)	C(37)	C(36)	C(35)	120.9(4)
C(16)	C(8)	C(9)	113.9(3)	C(36)	C(37)	C(38)	119.7(4)
C(22)	C(8)	C(9)	115.7(3)	C(37)	C(38)	C(39)	120.3(4)
C(22)	C(8)	C(16)	111.8(3)	C(38)	C(39)	C(34)	120.6(4)
N(1)	C(9)	C(8)	100.9(3)	C(41)	C(40)	C(32)	120.3(3)
N(1)	C(9)	C(10)	110.4(3)	C(45)	C(40)	C(32)	121.0(3)
C(10)	C(9)	C(8)	114.7(3)	C(45)	C(40)	C(41)	118.7(3)
C(11)	C(10)	C(9)	123.2(3)	C(42)	C(41)	C(40)	120.6(3)
C(11)	C(10)	C(15)	118.8(4)	C(41)	C(42)	C(43)	120.6(4)
C(15)	C(10)	C(9)	118.0(4)	C(44)	C(43)	C(42)	118.9(4)

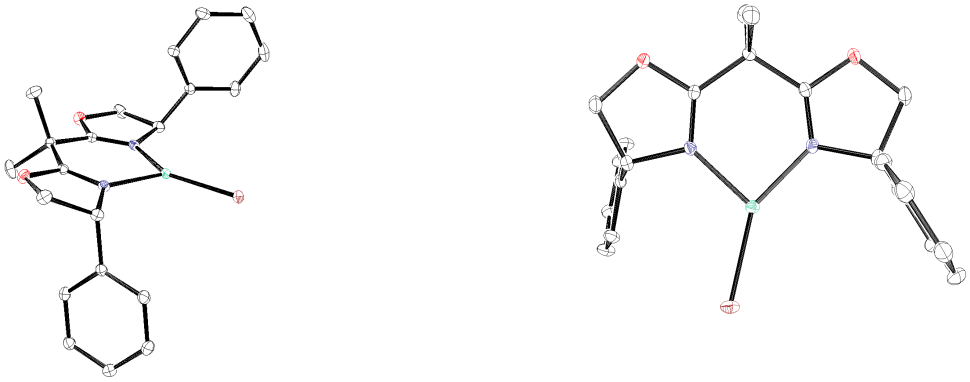
C(12) C(11) C(10)	120.4(4)	C(43)	C(44)	C(45)	121.0(4)
C(13) C(12) C(11)	120.7(4)	C(44)	C(45)	C(40)	120.2(4)
C(12) C(13) C(14)	119.3(4)	C(47)	C(46)	C(32)	120.6(3)
C(15) C(14) C(13)	120.6(4)	C(51)	C(46)	C(32)	120.3(3)
C(14) C(15) C(10)	120.3(4)	C(51)	C(46)	C(47)	119.0(4)
C(17) C(16) C(8)	122.9(3)	C(48)	C(47)	C(46)	120.5(4)
C(17) C(16) C(21)	119.1(4)	C(49)	C(48)	C(47)	120.1(4)
C(21) C(16) C(8)	117.8(3)	C(50)	C(49)	C(48)	120.1(4)
C(18) C(17) C(16)	120.1(4)	C(49)	C(50)	C(51)	120.1(4)
C(17) C(18) C(19)	120.6(4)	C(46)	C(51)	C(50)	120.2(4)
C(18) C(19) C(20)	119.5(4)	C(55)	O(00I)	C(52)	107.1(5)
C(21) C(20) C(19)	120.0(4)	O(00I)	C(52)	C(53)	106.2(5)
C(20) C(21) C(16)	120.8(4)	C(52)	C(53)	C(54)	104.8(6)
C(23) C(22) C(8)	118.1(3)	C(55)	C(54)	C(53)	100.7(6)
C(27) C(22) C(8)	122.9(3)	O(00I)	C(55)	C(54)	109.7(6)
C(27) C(22) C(23)	119.0(3)				

Table S–13. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for Ni^{II}PhBr(Ph-BOX^{Ph}).

Atom	*x*	*y*	*z*	U(eq)
H(2)	8065	3990	3162	26
H(3)	9556	2987	2906	36
H(4)	10125	1984	3462	36
H(5)	9253	1986	4259	39
H(6)	7656	2938	4500	31
H(9)	5637	5962	4477	19
H(11)	4561	4493	5375	31
H(12)	5433	4380	6178	37
H(13)	7054	5269	6472	39
H(14)	7713	6319	5970	40
H(15)	6840	6449	5170	33
H(17)	4807	6015	3758	28
H(18)	3992	6484	2999	35
H(19)	1805	7031	2943	39
H(20)	482	7181	3667	36
H(21)	1287	6709	4423	32
H(23)	4363	7379	4877	30
H(24)	3738	8234	5510	33
H(25)	2162	7846	6117	38
H(26)	1276	6585	6101	44
H(27)	1901	5719	5468	35
H(29A)	860	4497	4269	52
H(29B)	965	3760	3904	52
H(29C)	1676	4569	3754	52
H(30A)	3284	3250	4903	53
H(30B)	1843	3018	4658	53
H(30C)	1956	3775	5006	53
H(33)	6003	2687	3454	19
H(35)	4181	4433	3156	29
H(36)	4290	5079	2388	37
H(37)	5274	4478	1700	37
H(38)	6238	3242	1779	38
H(39)	6203	2600	2544	31
H(41)	2259	3107	2804	24
H(42)	1302	2658	2063	30

H(43)	1690	1375	1796	33
H(44)	3081	559	2272	37
H(45)	4001	990	3025	30
H(47)	6110	1472	3536	26
H(48)	6582	424	4067	34
H(49)	5053	104	4707	36
H(50)	3038	809	4804	36
H(51)	2499	1826	4246	30
H(52A)	2783	5904	6957	58
H(52B)	4036	5781	6575	58
H(53A)	4495	6050	7500	75
H(53B)	5519	5504	7183	75
H(54A)	4933	4649	7794	105
H(54B)	3404	5005	7845	105
H(55A)	4424	3991	7104	101
H(55B)	2919	3996	7345	101

Side view **Top view**



ORTEP plots (side and top views) of Ni^{I}Br(Ph-BOX) (**3**), with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table S–14. Crystal data and structure refinement for $Ni^{I}Br$(Ph-BOX).

Identification code	((*R*,*R*)-Ph-BOX)$Ni^{I}Br$
Empirical formula	$C_{21}H_{22}BrN_2NiO_2$
Formula weight	473.03
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.457(2)
b/Å	13.597(3)
c/Å	15.622(4)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2008.7(8)
Z	4
ρ_{calc}g/cm^3	1.564
μ/mm^{-1}	2.973
F(000)	964.0
Crystal size/mm^3	0.289 × 0.151 × 0.133
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.22 to 87.34
Index ranges	$-18 \le h \le 18$, $-26 \le k \le 22$, $-30 \le l \le 30$
Reflections collected	58562
Independent reflections	15114 [R_{int} = 0.0433, R_{sigma} = 0.0574]
Data/restraints/parameters	15114/0/246
Goodness-of-fit on F^2	0.988
Final R indexes [I>=2σ (I)]	R_1 = 0.0335, wR_2 = 0.0511
Final R indexes [all data]	R_1 = 0.0612, wR_2 = 0.0566
Largest diff. peak/hole / e Å^{-3}	0.53/-0.64
Flack parameter	0.006(4)

Table S–15. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ni^{I}Br$(Ph-BOX). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br(1)	6216.02(12)	9468.17(8)	3699.36(7)	23.29(3)
Ni(1)	6909.02(14)	7850.53(10)	3608.76(8)	16.32(3)
O(1)	8826.1(8)	5366.3(6)	2632.7(5)	22.19(15)
O(2)	5767.1(8)	5451.2(6)	5070.4(5)	21.60(15)
N(1)	7940.0(9)	6843.9(7)	2994.0(5)	17.13(16)
N(2)	6339.0(9)	6903.8(7)	4477.4(5)	16.75(15)
C(1)	8725.1(11)	7030.9(9)	2181.2(6)	19.90(19)
C(2)	9377.9(12)	6016.9(10)	1972.6(7)	25.6(2)
C(3)	8023.7(10)	5926.1(8)	3159.9(6)	16.70(17)
C(4)	7245.2(10)	5334.5(8)	3827.7(6)	16.81(18)
C(5)	8261.7(13)	4672.7(10)	4337.3(9)	31.0(3)
C(6)	6177.1(14)	4688.8(10)	3334.1(8)	28.5(2)
C(7)	6441.8(10)	5972.2(8)	4453.7(6)	16.16(17)
C(8)	4881.4(12)	6171.2(9)	5520.5(8)	23.9(2)
C(9)	5520.7(11)	7165.4(9)	5267.8(6)	18.89(18)
C(10)	7712.3(11)	7394.4(8)	1502.8(6)	18.29(19)
C(11)	7986.8(13)	8247.3(9)	1040.0(8)	25.9(2)
C(12)	7058.3(16)	8557.9(11)	398.4(9)	34.5(3)
C(13)	5846.6(14)	8026.1(11)	229.5(8)	31.7(3)
C(14)	5545.7(14)	7179.2(11)	693.3(7)	27.6(2)
C(15)	6480.7(11)	6867.8(9)	1322.6(7)	21.93(19)
C(16)	6509.3(10)	7620.7(8)	5917.8(6)	16.64(18)
C(17)	7521.5(11)	7051.9(8)	6346.5(8)	22.95(19)
C(18)	8417.0(12)	7476.6(9)	6948.5(8)	23.5(2)
C(19)	8308.7(13)	8468.7(9)	7132.9(8)	25.2(2)
C(20)	7342.7(14)	9044.0(9)	6690.3(9)	27.8(2)
C(21)	6456.2(12)	8621.2(9)	6084.6(8)	22.7(2)

Table S–16. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Ni^{I}Br$(Ph-BOX). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	30.22(5)	15.64(4)	24.01(5)	1.29(4)	-6.95(4)	3.18(4)
Ni(1)	19.66(5)	15.08(6)	14.22(5)	0.28(5)	-2.43(5)	0.84(5)
O(1)	23.3(3)	23.6(4)	19.7(3)	-1.0(3)	6.1(3)	5.2(3)
O(2)	24.0(3)	19.8(4)	21.0(4)	-0.3(3)	7.2(3)	-3.9(3)
N(1)	18.1(4)	20.5(4)	12.7(3)	0.4(3)	0.1(3)	0.7(3)
N(2)	18.2(4)	18.2(4)	13.8(3)	-0.9(3)	1.0(3)	2.6(3)
C(1)	18.2(4)	25.8(5)	15.6(4)	1.1(4)	2.4(3)	-3.0(4)
C(2)	24.4(5)	34.4(7)	18.0(5)	3.1(4)	4.6(4)	8.7(5)
C(3)	14.4(4)	21.2(5)	14.5(4)	-2.5(3)	-0.8(3)	1.9(4)
C(4)	16.5(4)	16.3(4)	17.7(4)	-0.1(3)	0.2(3)	1.3(3)
C(5)	24.0(5)	33.2(7)	35.8(6)	15.0(5)	5.7(5)	11.8(5)
C(6)	29.3(5)	29.7(6)	26.6(5)	-9.1(5)	3.2(5)	-9.9(5)
C(7)	15.1(4)	19.1(5)	14.3(4)	-0.1(3)	0.1(3)	-1.7(3)
C(8)	21.6(5)	27.4(6)	22.9(5)	-3.6(4)	7.3(4)	-3.5(4)
C(9)	17.1(4)	22.6(5)	17.0(4)	-1.7(4)	2.1(3)	2.2(4)
C(10)	22.3(4)	18.7(5)	13.9(4)	1.1(3)	4.1(3)	1.3(4)
C(11)	29.1(5)	21.4(5)	27.3(5)	5.6(4)	9.4(4)	0.7(5)
C(12)	45.2(8)	27.4(7)	31.0(6)	13.9(5)	10.7(6)	12.2(6)
C(13)	39.2(7)	36.1(8)	19.7(5)	2.6(5)	-0.2(4)	17.8(6)
C(14)	29.4(5)	33.5(7)	19.9(5)	-4.6(5)	-5.0(4)	5.3(5)
C(15)	26.4(5)	21.2(5)	18.2(4)	0.0(4)	-2.1(4)	-1.3(4)
C(16)	18.7(4)	18.0(5)	13.3(4)	0.1(3)	3.5(3)	2.4(3)
C(17)	27.1(5)	16.2(4)	25.5(5)	0.8(4)	-2.6(4)	3.1(4)
C(18)	24.3(5)	21.7(6)	24.6(5)	4.6(4)	-4.7(4)	-0.1(4)
C(19)	27.5(5)	23.5(6)	24.5(5)	-2.5(4)	-3.2(4)	-2.4(4)
C(20)	35.7(6)	16.3(5)	31.2(6)	-3.6(5)	-3.3(5)	4.2(5)
C(21)	26.5(5)	19.0(5)	22.6(5)	-0.5(4)	-1.2(4)	6.8(4)

Table S–17. Bond lengths for $Ni^{I}Br$(Ph-BOX).

Br(1)	Ni(1)	2.2994(5)	C(4)	C(7)	1.5118(14)
Ni(1)	N(1)	1.9355(9)	C(8)	C(9)	1.5324(17)
Ni(1)	N(2)	1.9466(9)	C(9)	C(16)	1.5128(15)
O(1)	C(2)	1.4554(15)	C(10)	C(11)	1.3910(16)
O(1)	C(3)	1.3540(12)	C(10)	C(15)	1.3958(15)
O(2)	C(7)	1.3554(13)	C(11)	C(12)	1.3978(18)
O(2)	C(8)	1.4678(14)	C(12)	C(13)	1.380(2)
N(1)	C(1)	1.4928(13)	C(13)	C(14)	1.3899(19)
N(1)	C(3)	1.2770(14)	C(14)	C(15)	1.3884(16)
N(2)	C(7)	1.2709(14)	C(16)	C(17)	1.4011(15)
N(2)	C(9)	1.5000(13)	C(16)	C(21)	1.3859(16)
C(1)	C(2)	1.5454(17)	C(17)	C(18)	1.3912(16)
C(1)	C(10)	1.5115(15)	C(18)	C(19)	1.3831(17)
C(3)	C(4)	1.5091(15)	C(19)	C(20)	1.3873(17)
C(4)	C(5)	1.5387(15)	C(20)	C(21)	1.3888(17)
C(4)	C(6)	1.5446(16)			

Table S–18. Bond angles /° for $Ni^{I}Br$(Ph-BOX).

N(1)	Ni(1)	Br(1)	148.27(3)	O(2)	C(7)	C(4)	113.36(9)
N(1)	Ni(1)	N(2)	91.02(4)	N(2)	C(7)	O(2)	117.66(9)
N(2)	Ni(1)	Br(1)	120.71(3)	N(2)	C(7)	C(4)	128.97(9)
C(3)	O(1)	C(2)	106.87(9)	O(2)	C(8)	C(9)	103.88(8)
C(7)	O(2)	C(8)	105.10(9)	N(2)	C(9)	C(8)	101.91(9)
C(1)	N(1)	Ni(1)	123.52(7)	N(2)	C(9)	C(16)	109.32(8)
C(3)	N(1)	Ni(1)	128.43(7)	C(16)	C(9)	C(8)	115.58(9)
C(3)	N(1)	C(1)	107.96(9)	C(11)	C(10)	C(1)	121.25(10)
C(7)	N(2)	Ni(1)	128.14(7)	C(11)	C(10)	C(15)	118.59(11)
C(7)	N(2)	C(9)	107.44(9)	C(15)	C(10)	C(1)	120.16(10)
C(9)	N(2)	Ni(1)	124.05(7)	C(10)	C(11)	C(12)	120.48(12)
N(1)	C(1)	C(2)	103.07(9)	C(13)	C(12)	C(11)	120.02(12)
N(1)	C(1)	C(10)	109.69(8)	C(12)	C(13)	C(14)	120.28(12)
C(10)	C(1)	C(2)	113.39(9)	C(15)	C(14)	C(13)	119.43(12)
O(1)	C(2)	C(1)	104.45(8)	C(14)	C(15)	C(10)	121.18(11)
O(1)	C(3)	C(4)	113.22(9)	C(17)	C(16)	C(9)	121.14(10)
N(1)	C(3)	O(1)	117.43(9)	C(21)	C(16)	C(9)	120.36(10)
N(1)	C(3)	C(4)	129.12(9)	C(21)	C(16)	C(17)	118.47(10)
C(3)	C(4)	C(5)	111.38(9)	C(18)	C(17)	C(16)	120.66(10)
C(3)	C(4)	C(6)	106.08(9)	C(19)	C(18)	C(17)	120.04(11)
C(3)	C(4)	C(7)	112.75(9)	C(18)	C(19)	C(20)	119.66(11)
C(5)	C(4)	C(6)	109.54(11)	C(19)	C(20)	C(21)	120.25(12)
C(7)	C(4)	C(5)	108.34(9)	C(16)	C(21)	C(20)	120.83(11)
C(7)	C(4)	C(6)	108.69(9)				

Table S–19. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for Ni^{I}Br(Ph-BOX).

Atom	*x*	*y*	*z*	U(eq)
H(1)	9489	7527	2279	24
H(2A)	9086	5792	1397	31
H(2B)	10423	6046	1996	31
H(5A)	8817	4271	3940	46
H(5B)	7716	4243	4717	46
H(5C)	8899	5083	4679	46
H(6A)	5544	5110	2999	43
H(6B)	5620	4301	3741	43
H(6C)	6689	4245	2949	43
H(8A)	4927	6072	6148	29
H(8B)	3884	6123	5333	29
H(9)	4750	7640	5121	23
H(11)	8811	8621	1161	31
H(12)	7261	9135	79	41
H(13)	5216	8240	-206	38
H(14)	4707	6817	581	33
H(15)	6279	6286	1636	26
H(17)	7597	6369	6225	28
H(18)	9103	7085	7233	28
H(19)	8893	8755	7560	30
H(20)	7287	9730	6802	33
H(21)	5805	9023	5781	27

X. Computational Details

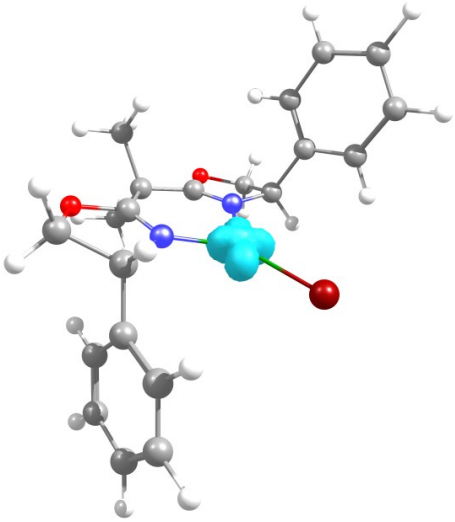
General computational methods. All calculations were performed with Gaussian 09 Rev B.01.[9] Unless otherwise noted, the gas-phase geometry optimizations were performed with the B3LYP hybrid functional and 6-31G* basis set for all atoms with spin state being the only restraint, followed by numerical frequency calculations at the same level of theory to characterize stationary points as minima (no imaginary frequencies) or transition states (one and only one imaginary frequency) on the potential energy surface. Intrinsic reaction coordinate (IRC) calculations were conducted to ensure the relevance of transition states to the corresponding intermediates. Exhaustive conformational searches were performed for all intermediates in order to map out the lowest energy profile. Thermal corrections for enthalpies and free energies at 213 K were obtained from frequency calculations. Free energies were corrected (1.21 kcal mol^{-1} at 213 K; 1.89 kcal mol^{-1} at 298 K) from standard state (1 bar) to solution state (1 M). Single-point energy calculations including solvent effects were performed using M06 functional with 6-311+G** basis set with SMD solvation model on optimized geometries. The choice of functional and basis sets was based on previous studies,[10] as well as our own efforts in benchmarking computationally optimized geometries to crystal structures.

Time-dependent DFT calculations were carried out at the B3LYP/6-31G* level of theory on optimized geometries. Natural transition orbital calculations[11] were carried out following td-DFT calculations to assist the assignment of transitions.

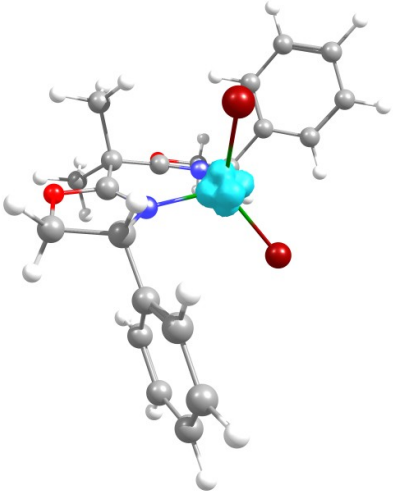
Spin density plots and natural transition orbital representations were rendered with Chemcraft.[12] Molecular geometries were rendered with CYLview.[13]

Calculated spin density plots:

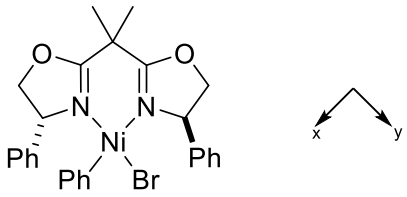
$Ni^{I}Br$(Ph-BOX) (**3**; S = ½)



$Ni^{II}Br_2$(Ph-BOX) (**1**; S = 1)

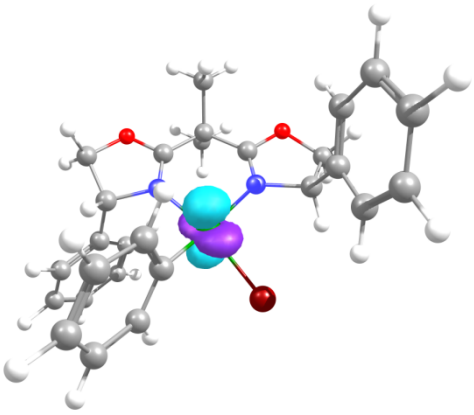


Time-dependent DFT results. Based on the crystal field splitting, the square planar Ni^{II}PhBr(Ph-BOX) and Ni^{II}PhBr(Ph-BOX^{Ph}) complexes should feature two absorptive d→d transitions as the lowest and the second-lowest energy transitions. The assignments are consistent with the results found from time-dependent DFT calculations. The td-DFT results for the first two electronic transitions are shown below in natural transition orbital representations. The axis used for the natural transition orbital representations is indicated:

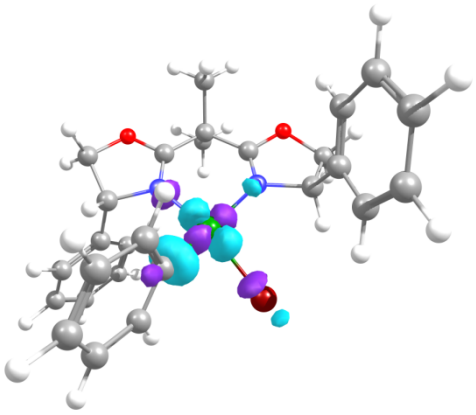


$Ni^{II}PhBr$ (Ph-BOX) (**2**):

Transition 1 ($dz^2 \rightarrow dx^2\text{-}y^2$)

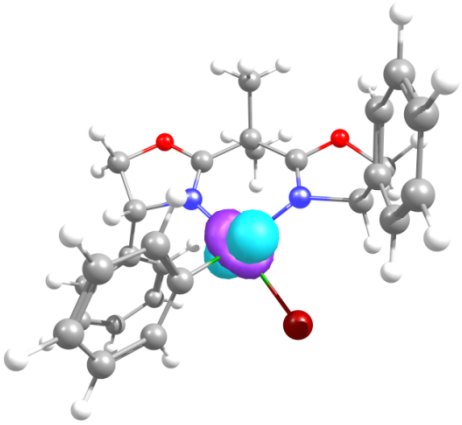


donor

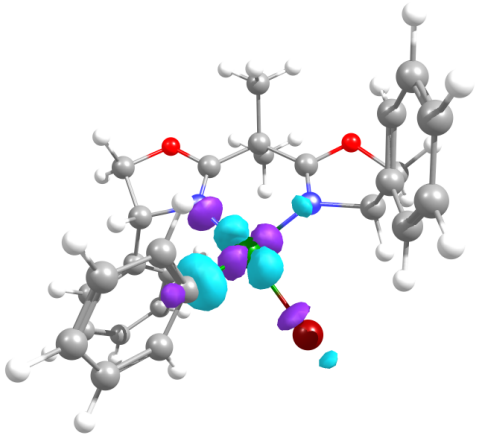


acceptor

Transition 2 ($dxy \rightarrow dx^2\text{-}y^2$)



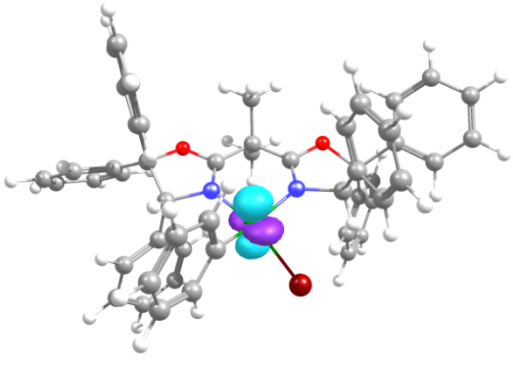
donor



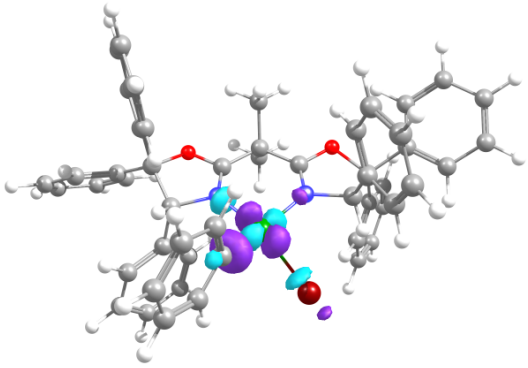
acceptor

$Ni^{II}PhBr$ (Ph-BOX^{Ph}) (**2^{Ph}**):

Transition 1 ($dz^2 \rightarrow dx^2\text{-}y^2$)

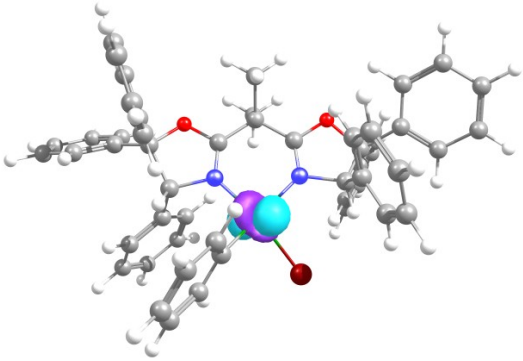


donor

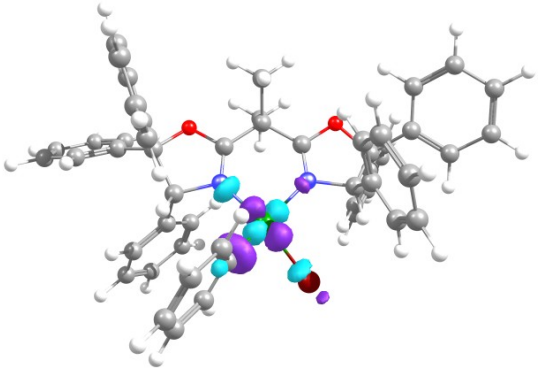


acceptor

Transition 2 ($dxy \rightarrow dx^2\text{-}y^2$)



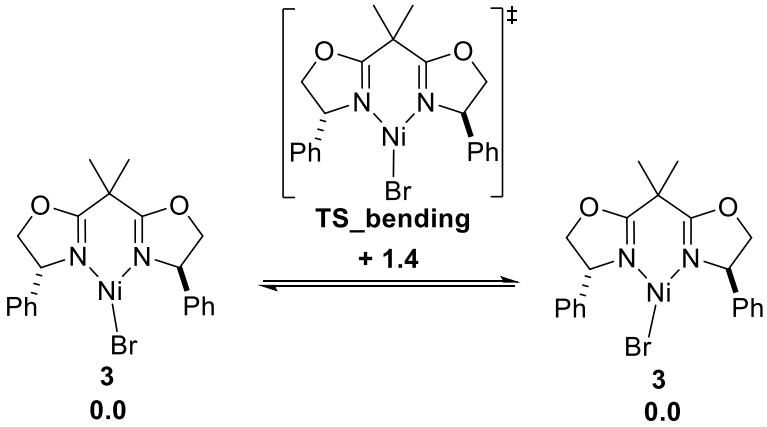
donor



acceptor

Bending of th Ni–Br bond in $Ni^{I}Br$(Ph-BOX) (3):

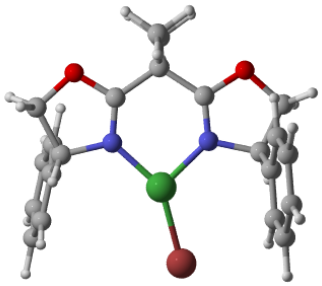
Relative ΔG_{213K} (kcal mol^{-1}):



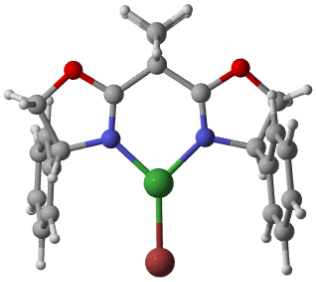
Computed relative free energies for the bending of the Ni–Br bond in Ni^{I}Br(Ph-BOX) (**3**), calculated at (U)M06/6-311+G**, SMD(THF) //(U)B3LYP/6-31G* level of theory.

Geometries:

Nickel complex **3**

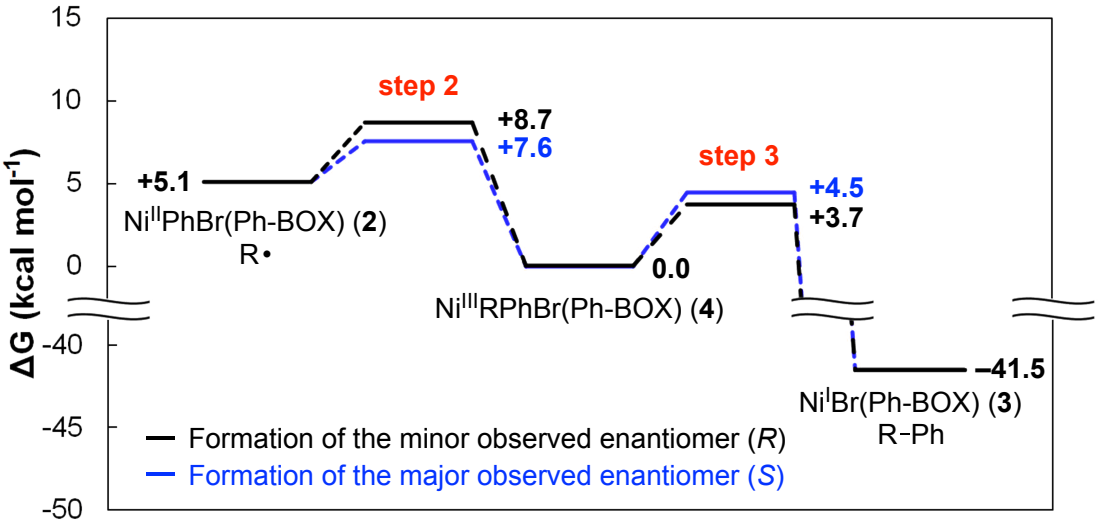


TS_bending



Radical recombination (RR) and reductive elimination (RE) steps:

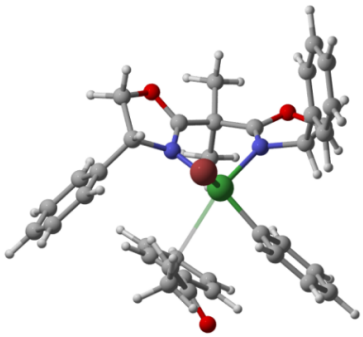
Relative ΔG_{213K} (kcal mol^{-1}):



Computed relative free energies for radical recombination (RR) and reductive elimination (RE) steps to form major (blue) and minor (black) enantiomers of the cross-coupling product. The DFT calculations were carried out at (U)M06/6-311+G**, SMD(THF)//(U)B3LYP/6-31G* level of theory.

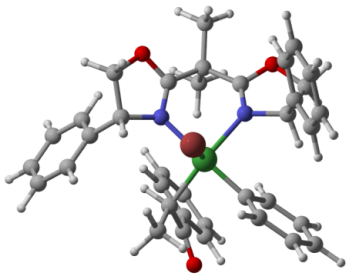
Geometries of intermediates and transition states along the major (in blue) and minor (in black) pathways:

TS-RR



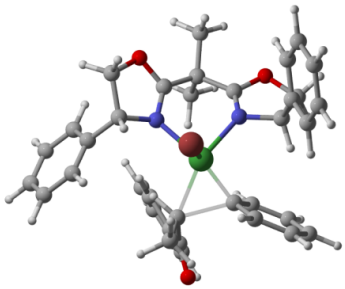
Ni–C(Ph) = 1.962 Å
Ni–C(R) = 3.018 Å
C–Ni–C = 73.66 °
Ni–Br = 2.429 Å

Nickel complex **4**



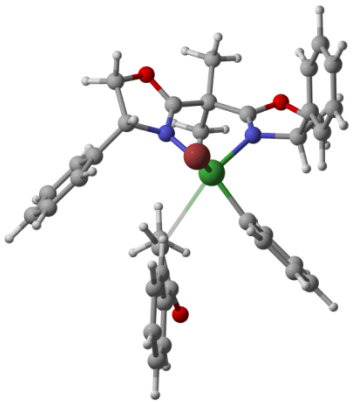
Ni–C(Ph) = 1.907 Å
Ni–C(R) = 2.023 Å
C–Ni–C = 84.93 °
Ni–Br = 2.508 Å

TS-RE



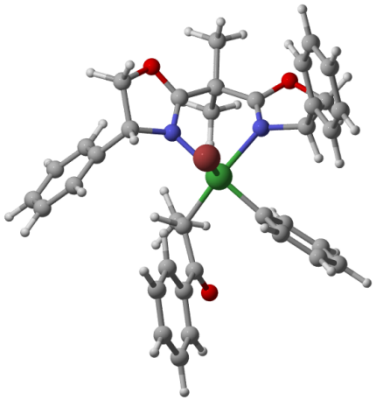
Ni–C(Ph) = 1.909 Å
Ni–C(R) = 2.201 Å
C–Ni–C = 59.00 °
Ni–Br = 2.460 Å

TS-RR'



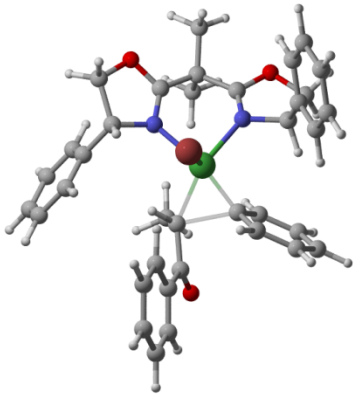
Ni–C(Ph) = 1.965 Å
Ni–C(R) = 3.038 Å
C–Ni–C = 71.47 °
Ni–Br = 2.428 Å

4'



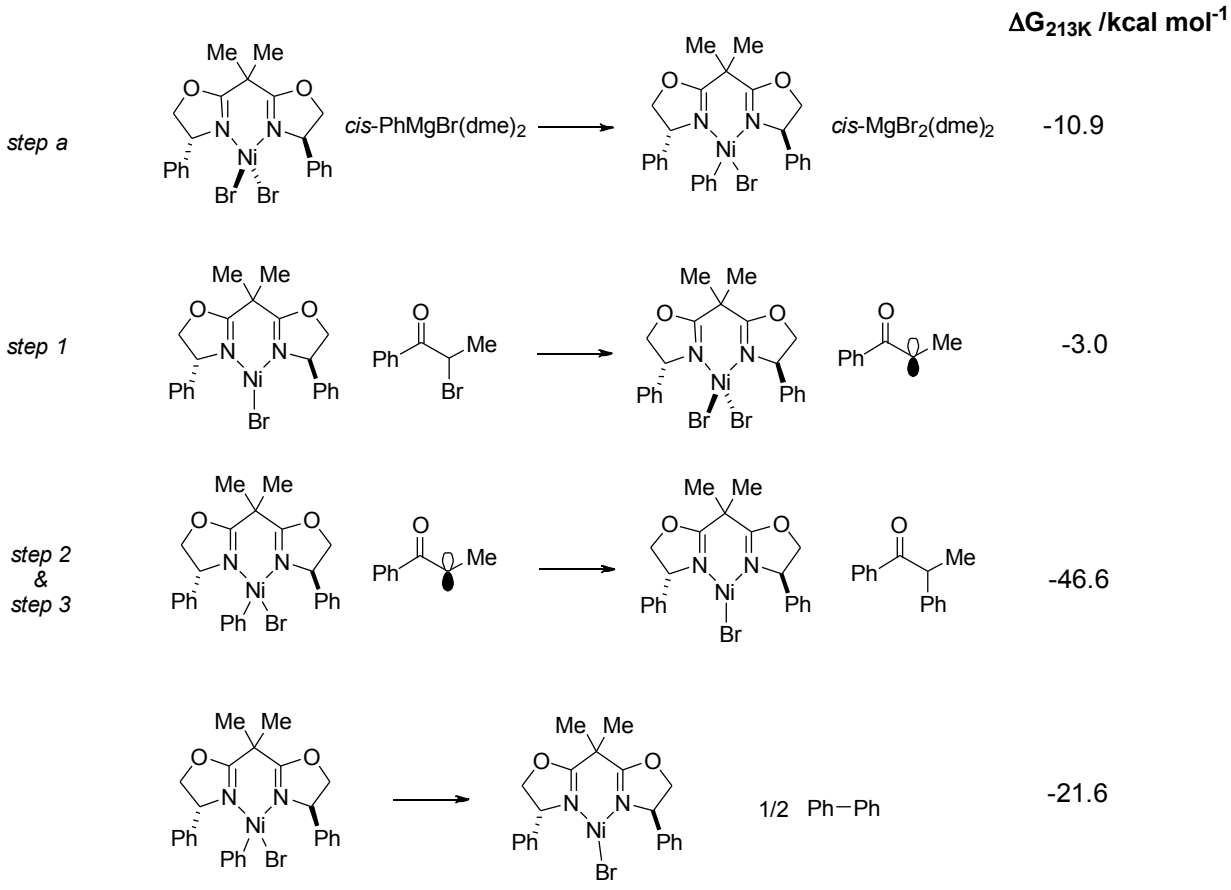
Ni–C(Ph) = 1.906 Å
Ni–C(R) = 1.995 Å
C–Ni–C = 85.13 °
Ni–Br = 2.509 Å

TS-RE'

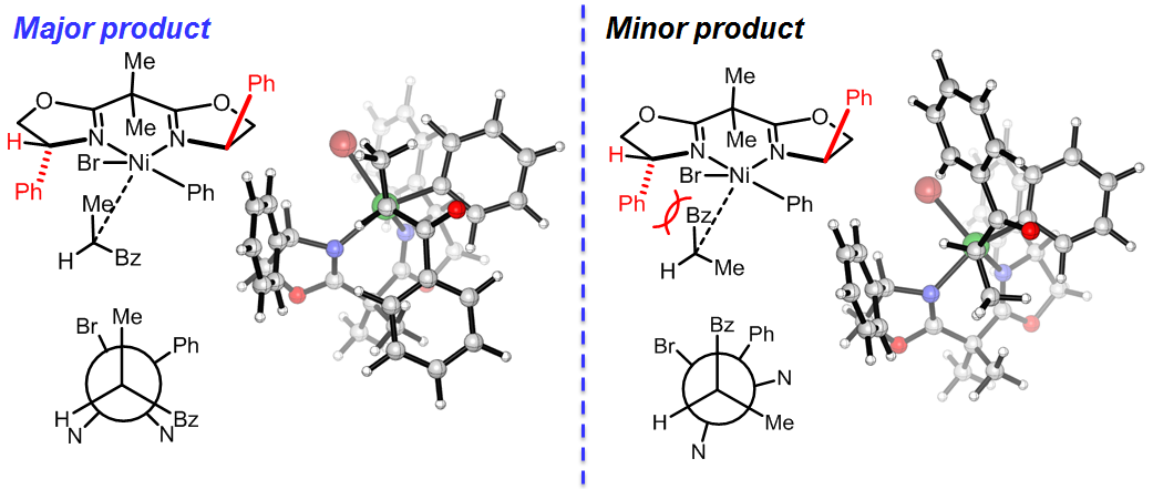


Ni–C(Ph) = 1.912 Å
Ni–C(R) = 2.148 Å
C–Ni–C = 59.72 °
Ni–Br = 2.473 Å

Computed free energies of the individual steps

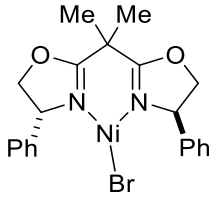


The structures of the computed transition states for the stereochemistry-determining steps are shown below. A plausible explanation for the stereoselectivity is evident from the Newman-type projections, viewed along the forming C–Ni bond: in the structure of the transition state that leads to the minor product, steric interactions of the benzoyl group lead to a higher-energy transition state.



(U)M06/6-311+G,SMD(THF)//(U)B3LYP/6-31G***

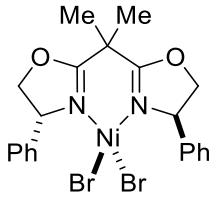
Coordinates of computed geometries:



3 Ni^{I}Br(Ph-BOX) doublet

O	2.02908900	2.38672600	-1.57338700
O	-1.86102200	2.77746200	1.25421200
N	1.19044000	0.50024400	-0.66504600
N	-1.16466100	0.69431800	0.72049900
C	1.08956800	1.77316800	-0.80656800
C	3.49984900	-0.32859500	-0.30669700
C	5.21612600	0.24279000	1.31513900
H	5.81167600	0.99690000	1.82312000
C	-0.98088700	1.96578300	0.60930100
C	4.27326100	0.63054500	0.36281900
H	4.13964400	1.68816900	0.14674900
C	-3.50570300	-0.13516500	0.67345300
C	2.79888600	1.31529800	-2.18530100
H	3.85085900	1.60018400	-2.16449800

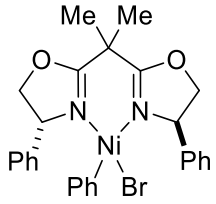
H	2.46244500	1.21622000	-3.22245800
C	-3.87848600	-1.46734500	0.87882400
H	-3.37502300	-2.05435700	1.64240200
C	2.45589700	0.07327900	-1.33587300
H	2.21735200	-0.78845600	-1.96231100
C	-2.41148400	0.48809800	1.51936400
H	-2.16759500	-0.18950700	2.34124900
C	5.39358300	-1.11022800	1.61333100
H	6.12954800	-1.41316900	2.35342300
C	-2.71066900	1.91223700	2.04763600
H	-3.74483700	2.22843300	1.90476700
H	-2.42907900	2.03790800	3.09784900
C	3.67512100	-1.68204900	0.00664900
H	3.04962900	-2.42769300	-0.47613100
C	0.06647800	2.70476700	-0.19609600
C	-4.87828100	-2.05317400	0.09968200
H	-5.15135000	-3.09119600	0.26667200
C	-4.14943900	0.60355500	-0.32992300
H	-3.86628900	1.63868600	-0.50873000
C	0.81393100	3.70258800	0.73245600
H	1.33013600	3.17143800	1.53891700
H	0.10099900	4.40215500	1.17520300
H	1.55320100	4.26300500	0.15463300
C	4.61789600	-2.06962400	0.96068100
H	4.74137400	-3.12344300	1.19463800
C	-5.14874300	0.02109500	-1.10785500
H	-5.63920000	0.60445900	-1.88255400
C	-5.51673200	-1.30995500	-0.89309600
H	-6.29432500	-1.76488200	-1.50056800
C	-0.65309100	3.48476200	-1.33259500
H	0.07939700	4.04423100	-1.91970700
H	-1.37521800	4.18372100	-0.90270400
H	-1.18380600	2.79694200	-1.99916000
Ni	-0.11564900	-0.69485700	0.02194100
Br	0.03060500	-2.93743400	-0.38576900



1 $Ni^{II}Br_2$(Ph-BOX) triplet

Br	-0.34301300	-2.26084000	-1.34456400
Br	0.40514000	-0.57140000	2.54683100
Ni	-0.02220500	-0.51151400	0.21097800
O	2.01652000	2.47440800	-1.83465700
O	-2.03152100	3.09260600	0.58552600
N	1.22535100	0.65236000	-0.79933200
N	-1.34576600	0.97894500	0.29127800
C	1.13105000	1.91540800	-0.98844300
C	3.43229000	-0.49849400	-0.71250100
C	5.21509700	-0.30695700	0.92308700
H	5.83718000	0.31153800	1.56423900
C	-1.08810800	2.22795100	0.16693400
C	4.24589700	0.28640100	0.11601900
H	4.11891400	1.36686900	0.14178200
C	-3.60238500	-0.13195800	0.27566800
C	2.81933500	1.38860000	-2.38323100
H	3.86954600	1.64564500	-2.23939800
H	2.59714200	1.32827900	-3.45153500
C	-4.18729400	-1.17248700	1.00437500
H	-3.92926300	-1.30490600	2.05218800
C	2.37037900	0.13013800	-1.59628100
H	1.96471800	-0.63441800	-2.26257000
C	-2.66186600	0.83215300	0.96720000
H	-2.43884000	0.45766400	1.97181000
C	5.37995500	-1.69438600	0.91193400
H	6.13373000	-2.15744700	1.54281700
C	-3.16972000	2.29676400	1.02037400
H	-3.99184200	2.48537500	0.32514000
H	-3.44654200	2.63165200	2.02132100
C	3.59672700	-1.88811600	-0.71128700
H	2.94531100	-2.50321200	-1.32587500

C	0.19006500	2.89274100	-0.30941400
C	-5.08685900	-2.04744800	0.39204800
H	-5.53025500	-2.85479500	0.96804700
C	-3.92373000	0.01692600	-1.08011800
H	-3.45762400	0.80697500	-1.66427600
C	0.92367800	3.43829000	0.95505600
H	1.13865000	2.62624700	1.65642100
H	0.29432400	4.18220700	1.45105000
H	1.86147500	3.91550400	0.65487600
C	4.56760800	-2.48298000	0.09683400
H	4.68249200	-3.56320900	0.09227300
C	-4.81737500	-0.85852300	-1.69372700
H	-5.04950600	-0.74144600	-2.74863100
C	-5.40433000	-1.89081500	-0.95703800
H	-6.09831000	-2.57525400	-1.43707500
C	-0.15793500	4.05491600	-1.27039900
H	0.75402400	4.57302900	-1.57233700
H	-0.82063600	4.76161400	-0.76771500
H	-0.65937200	3.68891700	-2.17241400

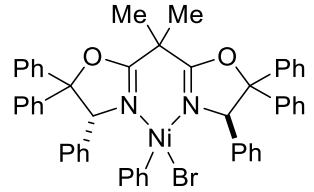


2 Ni^{II}PhBr(Ph-BOX) singlet

O	2.66918300	2.81231100	-0.72684500
O	-1.44320100	2.90433300	1.69615300
N	1.48831100	0.89661800	-0.62785200
N	-0.89660700	0.93280100	0.75124200
C	1.56505900	2.14045000	-0.32857600
C	3.63678800	-0.30790900	-0.26573100
C	5.05574700	-0.47006100	1.70184800
H	5.56040700	0.01122000	2.53559700
C	-0.58510000	2.16895200	0.95760700
C	4.29245000	0.29419600	0.81921200

H	4.21224200	1.36738600	0.97861200
C	-3.34756800	0.61973400	0.27946200
C	3.39832200	1.89094100	-1.58897000
C	-4.46464200	-0.18244800	0.54555800
H	-4.48756400	-0.78544100	1.44963200
C	2.80627100	0.51457200	-1.24045800
H	2.59097400	-0.07683200	-2.12976300
C	-2.25942500	0.72813900	1.33628100
H	-2.24041800	-0.18546000	1.92885000
C	5.17242400	-1.84913000	1.51188800
H	5.76746500	-2.44546000	2.19846800
C	-2.41965800	1.97496700	2.23138500
C	3.75377700	-1.69201000	-0.44443700
H	3.21838700	-2.16722800	-1.26065900
C	0.59133400	2.97586500	0.45960900
C	-5.53226600	-0.23530100	-0.35023000
H	-6.38798900	-0.86825300	-0.13147000
C	-3.31503800	1.36016700	-0.90753800
H	-2.44845700	1.96972000	-1.14550300
C	1.34040700	3.58133600	1.68051200
H	1.73594000	2.79142600	2.32765500
H	0.65387900	4.19941400	2.26300900
H	2.17290400	4.19785800	1.33449900
C	4.51850000	-2.45659000	0.43915300
H	4.59743500	-3.52971500	0.28862000
C	-4.37860000	1.30119900	-1.81010900
H	-4.33227900	1.87205600	-2.73351400
C	-5.49242100	0.50783500	-1.53185000
H	-6.31877200	0.46022400	-2.23576600
C	0.05625400	4.12169400	-0.44624600
H	0.89404000	4.73085700	-0.79414600
H	-0.63540400	4.75165800	0.11767800
H	-0.46663600	3.71880300	-1.31980900
Ni	0.01921200	-0.38670700	-0.27824900
C	-0.93676700	-1.80497800	0.49468300
C	-0.49632400	-2.15182900	1.78674400
C	-1.98555700	-2.56376200	-0.04728200
C	-1.07757200	-3.20244200	2.50734200

H	0.31607000	-1.59442700	2.25444200
C	-2.57961400	-3.60662400	0.66943900
H	-2.33757400	-2.34855800	-1.05207400
C	-2.12909600	-3.93252600	1.95168800
H	-0.70728900	-3.44885400	3.50097900
H	-3.39216300	-4.17405500	0.21929100
H	-2.58645300	-4.74886100	2.50607200
Br	0.48301800	-1.66182200	-2.16710300
H	3.19980500	2.18513700	-2.62466900
H	4.46046200	1.99443900	-1.36809500
H	-3.40141600	2.44425400	2.16982400
H	-2.15708700	1.78453200	3.27770400



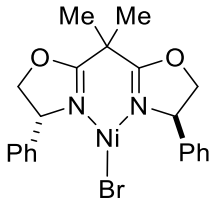
2^{Ph} $Ni^{II}PhBr(Ph\text{-}BOX^{Ph})$ singlet

O	-2.59122400	0.97026500	-1.65530900
O	2.18016000	0.87570900	-1.93257700
N	-1.46662200	0.12222300	0.09559800
N	1.27158200	-0.02329000	-0.08371100
C	-1.41823900	0.66396100	-1.06621700
C	-3.21003400	-1.62651700	0.22007100
C	-3.25202300	-3.67434600	-1.08709300
H	-3.06326300	-4.19069300	-2.02469500
C	1.08116100	0.56814500	-1.21591200
C	-2.96953900	-2.31339400	-0.97853500
H	-2.56752700	-1.78514100	-1.83816900
C	3.19978300	1.00887100	1.11465800
C	-3.62158100	0.85036800	-0.58729700
C	4.33633300	0.76194200	1.89585100
H	4.84144700	-0.19675600	1.81716100
C	-2.90633400	-0.14497000	0.38481400
H	-3.09771000	0.11731100	1.42189100

C	2.74837900	-0.05836200	0.12673700
H	3.01898000	-1.02687800	0.53771100
C	-3.77608300	-4.37164200	0.00432700
H	-3.99271800	-5.43330100	-0.07955300
C	3.29586700	0.10643200	-1.33416000
C	-3.72468400	-2.33704700	1.31095100
H	-3.86962600	-1.82531300	2.25763100
C	-0.20153300	1.00216400	-1.88706100
C	4.81565400	1.72341800	2.78383300
H	5.69701300	1.51114400	3.38290300
C	2.54171900	2.23519700	1.25730900
H	1.63981900	2.43966500	0.68949700
C	-0.31228900	0.28267800	-3.26109700
H	-0.35626100	-0.80364600	-3.13273400
H	0.56015900	0.52189300	-3.87263300
H	-1.21532400	0.61369600	-3.77927900
C	-4.00921400	-3.69976000	1.20419800
H	-4.40083800	-4.23593900	2.06423700
C	3.01420600	3.19714200	2.15248600
H	2.48275900	4.13909200	2.25771600
C	4.15532500	2.94693500	2.91460200
H	4.52082300	3.69399000	3.61395500
C	-0.15790500	2.54129200	-2.10567500
H	-1.07711600	2.86363000	-2.60023400
H	0.69796700	2.80512900	-2.73135900
H	-0.07778400	3.07228500	-1.15179400
Ni	0.00364200	-0.48848800	1.26205600
C	1.19087200	-1.64080100	2.14974300
C	1.23594400	-2.94120200	1.61018500
C	1.99206400	-1.38909200	3.27428000
C	2.05342700	-3.93908200	2.15678400
H	0.61647500	-3.19619500	0.74994800
C	2.82035400	-2.37554100	3.81867500
H	1.96152200	-0.41081900	3.74568800
C	2.85784000	-3.65655900	3.26167900
H	2.05552300	-4.93727600	1.72202100
H	3.42980500	-2.14511800	4.69066900
H	3.49599000	-4.42599600	3.69005000

Br	-1.21694300	-0.18143500	3.22257100
C	4.57546900	0.91674300	-1.46516600
C	5.81091800	0.27603400	-1.29450300
C	4.55573900	2.29175000	-1.72311900
C	7.00097200	0.99831300	-1.36961100
H	5.84232700	-0.79406300	-1.11055100
C	5.74901200	3.01161000	-1.80997400
H	3.60761800	2.79896000	-1.85859800
C	6.97447900	2.36987700	-1.63068800
H	7.94928300	0.48603500	-1.23185600
H	5.71668400	4.07798000	-2.01673000
H	7.90189400	2.93217300	-1.69678700
C	3.36687000	-1.19845300	-2.14215900
C	3.69412400	-1.09616900	-3.50601200
C	3.08547300	-2.46372400	-1.61465400
C	3.74019400	-2.22535200	-4.31831200
H	3.91788700	-0.12029600	-3.92702700
C	3.13914100	-3.59933800	-2.43123200
H	2.81349100	-2.59535700	-0.57318300
C	3.46474100	-3.48649900	-3.78057600
H	3.99709100	-2.12298300	-5.36929800
H	2.92056100	-4.57231200	-1.99996000
H	3.50586700	-4.37096400	-4.41059900
C	-3.77823900	2.26778100	-0.01209400
C	-3.20097000	2.67022700	1.20147900
C	-4.47103400	3.22167400	-0.77681800
C	-3.32877200	3.99305100	1.63799400
H	-2.64638500	1.97662100	1.82668300
C	-4.59068100	4.53923600	-0.34175900
H	-4.92501200	2.92485200	-1.71742400
C	-4.02080600	4.92994800	0.87295700
H	-2.88110100	4.28181700	2.58495200
H	-5.13478500	5.25883300	-0.94786200
H	-4.11926800	5.95550400	1.21899400
C	-4.91595300	0.34434400	-1.19841600
C	-6.02755900	0.17027700	-0.36109800
C	-5.04288700	0.06026100	-2.56143200
C	-7.23619500	-0.29308700	-0.87567900

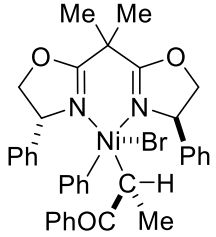
H	-5.94728600	0.40375900	0.69711500
C	-6.25871700	-0.39709400	-3.07773000
H	-4.19294800	0.19818000	-3.22006700
C	-7.35685600	-0.57838900	-2.23847300
H	-8.08575500	-0.42810300	-0.21192700
H	-6.34230900	-0.61118700	-4.13999300
H	-8.30075100	-0.93613800	-2.64055500



TS_bending

O	-1.92736600	2.58679400	1.45124000
O	1.92826100	2.58400100	-1.45372500
N	-1.16627200	0.59298400	0.71396700
N	1.16635900	0.59162500	-0.71354600
C	-1.02472600	1.87231300	0.72712900
C	-3.50045100	-0.21799000	0.51343800
C	-5.23697700	0.20377000	-1.13181900
H	-5.82473700	0.90812200	-1.71464200
C	1.02525500	1.87094300	-0.72869200
C	-4.26476100	0.67596600	-0.25009300
H	-4.09979400	1.74758700	-0.16354300
C	3.50037100	-0.21917000	-0.51066800
C	-2.71652800	1.61015400	2.17998700
H	-3.76091500	1.92056400	2.14140900
H	-2.36989000	1.60958800	3.21852100
C	3.71532000	-1.59414300	-0.35991600
H	3.10279000	-2.29791900	-0.91626800
C	-2.42194900	0.27515200	1.46258500
H	-2.18646300	-0.51477400	2.17925500
C	2.42222400	0.27223400	-1.46115400
H	2.18687300	-0.51905200	-2.17635400
C	-5.45315500	-1.16992300	-1.26482700

H	-6.21119100	-1.53828000	-1.95086600
C	2.71708100	1.60587100	-2.18092400
H	3.76154200	1.91610500	-2.14306800
H	2.37024200	1.60359500	-3.21939100
C	-3.71644600	-1.59317200	0.36624500
H	-3.10457500	-2.29598800	0.92453300
C	0.00028700	2.71326100	-0.00155200
C	4.68616900	-2.06572000	0.52551700
H	4.83761100	-3.13587200	0.63476100
C	4.26528600	0.67618300	0.25061200
H	4.10110000	1.74769900	0.16134900
C	-0.74814600	3.60711900	-1.03007200
H	-1.28314900	2.99291100	-1.76181700
H	-0.03262700	4.23966100	-1.56104800
H	-1.47104400	4.24227400	-0.51178200
C	-4.68765000	-2.06633700	-0.51795200
H	-4.83986900	-3.13665400	-0.62444700
C	5.23714400	0.20554500	1.13357800
H	5.82539700	0.91096900	1.71460600
C	5.45233200	-1.16795300	1.27010000
H	6.21010500	-1.53509900	1.95708200
C	0.74879000	3.60893300	1.02533100
H	0.03331700	4.24248400	1.55515700
H	1.47173200	4.24308800	0.50588300
H	1.28376200	2.99602500	1.75818900
Ni	-0.00086600	-0.70758400	0.00022800
Br	0.00055600	-2.99461400	-0.00280300



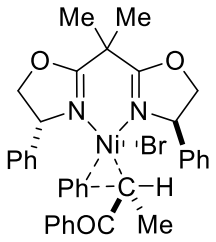
4 doublet

O	-0.73360200	-3.55384600	0.93471600

O	2.01640600	-0.70923600	3.23218800
N	-0.83715100	-1.48455700	0.05901700
N	1.49118600	-0.17646900	1.10809700
C	-0.52481500	-2.23106400	1.05675900
C	-2.97583200	-2.17493600	-1.08066400
C	-5.20726100	-2.25125400	-0.11680800
H	-5.85210600	-2.42090600	0.74137500
C	1.19843300	-0.83935600	2.16794100
C	-3.82565600	-2.39011100	0.01553800
H	-3.40719700	-2.67604900	0.97788800
C	3.94583600	-0.25785500	0.57822200
C	-1.07415200	-3.77430300	-0.46651200
C	4.67362000	0.44540000	-0.38647800
H	4.39961500	1.47047100	-0.61976900
C	-1.47295200	-2.37254900	-0.96994300
H	-0.98803500	-2.15838300	-1.92349400
C	2.83788900	0.44500100	1.34379500
H	2.79082000	1.48730500	1.03553500
C	-5.76120100	-1.89759800	-1.35005900
H	-6.83709700	-1.78694400	-1.45276500
C	2.97033100	0.33207300	2.87685100
C	-3.54288000	-1.82671300	-2.31270700
H	-2.89531700	-1.65585200	-3.16869600
C	0.02813200	-1.77661200	2.39717900
C	5.72974600	-0.16674900	-1.06363300
H	6.28167000	0.39028500	-1.81577000
C	4.29414600	-1.58678900	0.85626100
H	3.74153700	-2.15061200	1.60466700
C	-1.07606900	-1.01341500	3.18052200
H	-1.45153800	-0.15507500	2.61901500
H	-0.67079800	-0.66514300	4.13528700
H	-1.91405400	-1.68723800	3.38825100
C	-4.92600500	-1.68712200	-2.44762200
H	-5.34777300	-1.41076900	-3.40993000
C	5.34683600	-2.20028100	0.17986600
H	5.60307100	-3.23278400	0.40215800
C	6.06879400	-1.49007800	-0.78265600
H	6.88817700	-1.96874300	-1.31215200

C	0.50211500	-2.99056100	3.23135800
H	-0.33628400	-3.66906000	3.40295600
H	0.88547800	-2.64737500	4.19362700
H	1.29053000	-3.54879500	2.71915700
Ni	0.17178800	0.29063100	-0.45283400
C	0.92112300	2.03900100	-0.58778400
C	0.77267900	2.91331700	0.49987200
C	1.73868000	2.43181400	-1.65231500
C	1.44257900	4.14137700	0.53418900
H	0.12295100	2.65442600	1.33412500
C	2.40622500	3.66177800	-1.62089600
H	1.87034200	1.77075700	-2.50238900
C	2.26549400	4.51932100	-0.52792400
H	1.31155500	4.80302300	1.38791600
H	3.03716200	3.94860500	-2.45944300
H	2.78207900	5.47560100	-0.50877500
Br	1.44008600	-1.03656100	-2.16095200
H	-0.17571800	-4.15194500	-0.96208200
H	-1.87576500	-4.51188000	-0.50189500
H	3.95504800	0.01262400	3.21723500
H	2.66686400	1.24556100	3.39859200
C	-1.38855400	1.07560800	-1.47252800
H	-2.09505700	0.27662300	-1.23766800
C	-1.16291900	1.15548700	-2.97670700
H	-0.45850100	1.95033900	-3.22902800
H	-0.77657700	0.21563000	-3.37479100
H	-2.10980600	1.39751000	-3.48066100
C	-1.92837000	2.37064300	-0.93700900
C	-2.65595200	2.41002800	0.39083800
C	-3.21869900	1.28412900	1.00931000
C	-2.82569600	3.66648400	0.99650800
C	-3.93202700	1.41323300	2.20485400
H	-3.13164000	0.30484400	0.55204000
C	-3.52021300	3.79310900	2.19628400
H	-2.40491100	4.53137700	0.49450100
C	-4.07900100	2.66436900	2.80492600
H	-4.38197600	0.53420000	2.65992800
H	-3.63550200	4.77174300	2.65527600

H	-4.63191900	2.76234800	3.73576000
O	-1.82119000	3.41989100	-1.56266000

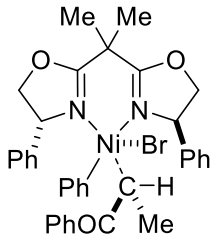


TS-RE

O	-0.45124100	-3.71059800	0.80354800
O	2.14945800	-0.72238700	3.17546800
N	-0.74562000	-1.60431400	0.05630000
N	1.59863200	-0.22824100	1.04945700
C	-0.32938000	-2.38141700	0.98873400
C	-2.82035400	-2.26119900	-1.17182200
C	-5.09173700	-2.46127700	-0.32897800
H	-5.77739300	-2.77554000	0.45349200
C	1.35401200	-0.92116700	2.10085100
C	-3.72028600	-2.65763400	-0.17065900
H	-3.34693500	-3.12517700	0.73833000
C	4.03216700	-0.05868800	0.51202500
C	-0.91163200	-3.89073600	-0.56606900
C	4.63416100	0.69633100	-0.49898300
H	4.23731500	1.67888700	-0.73777800
C	-1.32516200	-2.47051900	-1.01814600
H	-0.81572100	-2.20378200	-1.94730900
C	2.86940300	0.52174800	1.29894200
H	2.71423100	1.56031400	1.00774400
C	-5.58389900	-1.86301800	-1.49261100
H	-6.65220500	-1.70804500	-1.61532700
C	3.01488600	0.39718100	2.83156600
C	-3.32442100	-1.66750900	-2.33527000
H	-2.63589300	-1.36278100	-3.11957500
C	0.26240000	-1.95469200	2.32294000
C	5.72370200	0.18964300	-1.20965400

H	6.17705800	0.78567200	-1.99689700
C	4.53815800	-1.33415900	0.79960400
H	4.08307300	-1.93739600	1.58232800
C	-0.85507500	-1.31707300	3.19515400
H	-1.32125600	-0.46649800	2.69207600
H	-0.43219600	-0.98167700	4.14662400
H	-1.62883300	-2.06314100	3.40507500
C	-4.69811500	-1.46711900	-2.49488900
H	-5.07312800	-1.00300800	-3.40281200
C	5.62488400	-1.84253200	0.09011300
H	6.00525200	-2.83392200	0.32172000
C	6.22187600	-1.07972400	-0.91681400
H	7.06784200	-1.47630500	-1.47172800
C	0.86605000	-3.16972800	3.06751100
H	0.09006800	-3.91766600	3.24446400
H	1.27492500	-2.84643800	4.02635100
H	1.66406900	-3.64051000	2.48652400
Ni	0.28705000	0.22666700	-0.47805600
C	0.50651900	2.12261000	-0.49346500
C	0.33055800	2.73374100	0.77090800
C	1.41189400	2.73669100	-1.38323600
C	1.07095500	3.85551200	1.14857800
H	-0.39982600	2.33741700	1.47143500
C	2.14151100	3.86475300	-1.00700800
H	1.57055700	2.30116800	-2.36281400
C	1.98317500	4.43215100	0.26186400
H	0.91546200	4.29082500	2.13350500
H	2.84130900	4.30379900	-1.71475000
H	2.54590000	5.31724200	0.54553200
Br	1.41563700	-0.76827900	-2.42449500
H	-0.07028900	-4.28359900	-1.14262300
H	-1.72870800	-4.61324300	-0.55139300
H	4.02343600	0.15478800	3.16661200
H	2.64083500	1.27746500	3.36364600
C	-1.22477800	1.53553000	-1.39801800
H	-1.66732800	0.53923500	-1.27875600
C	-1.03761500	1.82937300	-2.88038800
H	-0.71294500	2.85968700	-3.03437900

H	-0.31969200	1.14122900	-3.33084200
H	-2.00144100	1.71277100	-3.39449200
C	-2.12471400	2.55579600	-0.74699700
C	-2.91568900	2.23329800	0.49678700
C	-3.19578500	0.93132600	0.93431900
C	-3.44904800	3.31762300	1.21476300
C	-3.99130700	0.72050900	2.06400000
H	-2.82068200	0.07200200	0.39166000
C	-4.22582200	3.10760800	2.35019800
H	-3.24124100	4.31890300	0.85278900
C	-4.50214100	1.80494200	2.77817700
H	-4.21976500	-0.29542800	2.37526600
H	-4.62399900	3.95706000	2.89908000
H	-5.11780200	1.63805900	3.65840400
O	-2.24270900	3.67418100	-1.23436300

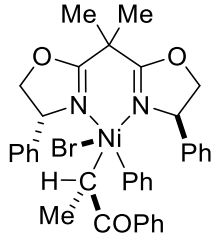


TS-RR

O	-0.37348600	-3.17420800	2.11083900
O	2.20608600	0.38243000	3.29177700
N	-0.44186300	-1.60140400	0.50136900
N	1.68547300	0.17841600	1.11604800
C	-0.21177000	-1.89467600	1.73069800
C	-2.25851300	-2.79301400	-0.76871700
C	-4.67172300	-2.73578400	-0.48707700
H	-5.53960200	-2.71323500	0.16667300
C	1.40410400	-0.11606900	2.33198900
C	-3.38882700	-2.75915300	0.06119200
H	-3.26887000	-2.75168200	1.14282400
C	4.09733400	0.13790600	0.49654500
C	-0.66405100	-3.93445000	0.90431700

C	4.57737200	0.48309200	-0.77100200
H	4.12075200	1.31013600	-1.30783200
C	-0.85516200	-2.85951900	-0.19522900
H	-0.14727500	-3.00087500	-1.01428700
C	2.96927800	0.94299900	1.11528000
H	2.80745000	1.85003800	0.53261900
C	-4.83961100	-2.74353700	-1.87487500
H	-5.83841900	-2.72570200	-2.30207500
C	3.14207600	1.27470800	2.61552400
C	-2.43636500	-2.79861500	-2.15758400
H	-1.56251200	-2.80612600	-2.80349000
C	0.22247800	-0.93231400	2.82805100
C	5.61902500	-0.24072200	-1.35376100
H	5.97856400	0.03477600	-2.34110300
C	4.66999300	-0.95051900	1.16938300
H	4.30342400	-1.23828900	2.15295700
C	-0.94326300	0.04747000	3.14350600
H	-1.26433500	0.59768400	2.25637600
H	-0.62322200	0.76152500	3.90826800
H	-1.80223200	-0.50968200	3.52943400
C	-3.72027000	-2.77391500	-2.70766800
H	-3.84327900	-2.77769000	-3.78712200
C	5.71042400	-1.67439100	0.58837100
H	6.14728900	-2.51529400	1.12054000
C	6.18914500	-1.31801300	-0.67502800
H	6.99977400	-1.88177700	-1.12875500
C	0.61438200	-1.69883500	4.11073200
H	-0.23936700	-2.27671900	4.47128500
H	0.91403300	-0.98880300	4.88362400
H	1.44269100	-2.39010800	3.93338700
Ni	0.42214300	0.06692700	-0.47090800
C	0.62553000	1.95582400	-0.96174200
C	0.44187000	2.94983600	0.02031900
C	1.14652300	2.38615800	-2.19450500
C	0.74973800	4.29496700	-0.20944300
H	0.03545600	2.68345000	0.99763300
C	1.46188200	3.72750700	-2.43727400
H	1.31011700	1.65780400	-2.98468300

C	1.26568800	4.68973500	-1.44496600
H	0.58473400	5.03286700	0.57397800
H	1.86142600	4.02117300	-3.40617800
H	1.50531300	5.73357800	-1.63327200
Br	1.31563400	-1.20149600	-2.33956100
H	0.19241600	-4.58795900	0.71898900
H	-1.55300100	-4.53709300	1.09549100
H	4.13857700	1.07013800	3.00695900
H	2.84595000	2.29922400	2.85817000
C	-2.20433200	0.91461200	-1.69229500
H	-2.33052600	-0.03209100	-1.17672400
C	-1.86020800	0.89663700	-3.14118100
H	-1.63264400	1.90672900	-3.48752900
H	-1.01450600	0.23178400	-3.34630100
H	-2.71849900	0.52105500	-3.72325900
C	-2.68141500	2.12931200	-1.06514500
C	-3.23857700	2.08262200	0.33619200
C	-3.87487200	0.95279300	0.87115600
C	-3.18138300	3.25583900	1.10556400
C	-4.43515700	0.99420100	2.15054800
H	-3.96386600	0.04680700	0.27999000
C	-3.72073100	3.29027100	2.38957700
H	-2.71207900	4.13089600	0.66799200
C	-4.35234100	2.15872000	2.91641300
H	-4.94580700	0.11855600	2.54453100
H	-3.66097600	4.20247600	2.97791500
H	-4.78696400	2.18966900	3.91241100
O	-2.64785500	3.21952300	-1.65617700



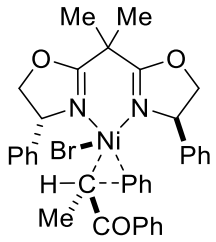
4' doublet

O	-0.72039300	3.94309200	-0.82554900

O	-3.72156100	1.59245700	1.68284400
N	0.17546600	1.98627400	-0.16920300
N	-2.05601400	0.43629500	0.70359400
C	-0.72245500	2.88602300	0.00739600
C	2.45005400	2.86861300	-0.80326100
C	3.91025200	4.29361900	0.51763300
H	4.03335100	5.09247900	1.24405200
C	-2.49390800	1.56613400	1.12613000
C	2.62999600	3.90056500	0.12968200
H	1.76452900	4.40346300	0.55569400
C	-3.78392000	-0.90501400	-0.51971100
C	0.24729400	3.62814100	-1.86900100
C	-3.73335500	-2.22755500	-0.97039600
H	-3.21497400	-2.97433800	-0.37548200
C	1.06597200	2.45946000	-1.27745200
H	1.14135600	1.63875000	-1.99295300
C	-3.18150800	-0.54534100	0.82742600
H	-2.79619800	-1.44523900	1.30352000
C	5.03212500	3.66155200	-0.02559100
H	6.02982000	3.96607900	0.27831000
C	-4.15096700	0.20264000	1.76928600
C	3.58081800	2.24648500	-1.34528200
H	3.45464900	1.44606000	-2.07015300
C	-1.78678000	2.90889100	1.09373900
C	-4.32332000	-2.58602800	-2.18371300
H	-4.27035900	-3.61643800	-2.52428900
C	-4.43547600	0.05596500	-1.30496600
H	-4.48572900	1.09019700	-0.97105300
C	-1.11250500	3.14787800	2.47444100
H	-0.36728300	2.38066200	2.69639900
H	-1.87493700	3.14156200	3.25921500
H	-0.61870600	4.12508100	2.48153500
C	4.86472800	2.63806400	-0.95866800
H	5.73093700	2.13999400	-1.38517800
C	-5.02326100	-0.29949600	-2.51764300
H	-5.52210500	0.45635600	-3.11846700
C	-4.96941700	-1.62385200	-2.95967900
H	-5.42566700	-1.90122600	-3.90612000

C	-2.81735700	4.03058200	0.82762900
H	-2.31175000	4.99842800	0.80740200
H	-3.56669900	4.03646100	1.62096200
H	-3.32496000	3.89326500	-0.13093100
Ni	-0.03389800	-0.03272100	0.40182300
C	-0.27436700	-1.69845700	1.29572000
C	-0.53954300	-1.67230300	2.67220100
C	-0.35917600	-2.92203700	0.62139500
C	-0.91837000	-2.83227100	3.35548300
H	-0.45174800	-0.74557600	3.23726600
C	-0.73291400	-4.08511500	1.30551900
H	-0.13946800	-2.96912800	-0.43983400
C	-1.01975700	-4.04504000	2.67127900
H	-1.12179600	-2.78758100	4.42320600
H	-0.79071600	-5.02715800	0.76450700
H	-1.30495700	-4.95090200	3.20023800
Br	-0.24533000	-0.61268700	-2.02955400
H	-0.31898400	3.33645200	-2.75799500
H	0.82965000	4.52829600	-2.06599600
H	-5.19543600	0.15704700	1.46140700
H	-4.05060000	-0.10574600	2.81470100
C	1.88359800	-0.22773500	0.91546400
H	2.34023100	0.20012500	0.01923900
C	2.03045300	0.71723200	2.11208100
H	3.07984700	0.75925100	2.43197500
H	1.71648900	1.73346100	1.86721800
H	1.47064700	0.35849900	2.98176300
C	2.54269700	-1.54623500	1.23502300
C	3.11070400	-2.41582800	0.14354200
C	2.94362500	-2.16429600	-1.22576000
C	3.87853400	-3.52377000	0.54127100
C	3.53189800	-3.00440700	-2.17386000
H	2.31448700	-1.34883600	-1.56424300
C	4.47070200	-4.35557400	-0.40384200
H	3.99520600	-3.70597300	1.60434000
C	4.30024900	-4.09613800	-1.76796100
H	3.38011300	-2.80577700	-3.23166700
H	5.06462700	-5.20715100	-0.08110500

H	4.76042900	-4.74577900	-2.50865800
O	2.71372700	-1.87992200	2.40525900

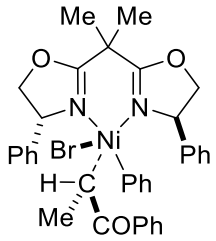


TS-RE'

O	-1.15486800	3.94165000	-1.02790800
O	-3.89837000	1.28354100	1.66195000
N	-0.09755600	2.10916700	-0.25142700
N	-2.15048800	0.29735900	0.64280600
C	-1.10657700	2.89561300	-0.17804700
C	2.16572900	3.02588900	-0.78940200
C	3.56542700	4.41399300	0.63123600
H	3.65838500	5.20771900	1.36774100
C	-2.71914000	1.38753500	1.00705200
C	2.30544700	4.04967000	0.15878300
H	1.42296300	4.56326600	0.53479300
C	-3.70607100	-1.40575600	-0.31570200
C	-0.01919900	3.79755100	-1.92531200
C	-3.42246900	-2.72500700	-0.68143100
H	-2.73282600	-3.30905500	-0.07840400
C	0.80212500	2.62788800	-1.32324000
H	0.91440200	1.82057200	-2.05183400
C	-3.09414700	-0.82255900	0.94615200
H	-2.53746500	-1.59809500	1.47284300
C	4.70657200	3.75714800	0.16120100
H	5.68858300	4.03893900	0.53104800
C	-4.10991100	-0.13831600	1.88896200
C	3.31455000	2.37688300	-1.25635500
H	3.21803800	1.58061300	-1.99039100
C	-2.24992300	2.82094700	0.82124300
C	-4.00272700	-3.28483100	-1.82117600

H	-3.76811900	-4.30932400	-2.09670700
C	-4.58009000	-0.65256600	-1.11191800
H	-4.81109900	0.37639600	-0.84433900
C	-1.74574500	3.35899600	2.19116700
H	-0.89864900	2.77369300	2.55938300
H	-2.55459000	3.31424000	2.92596900
H	-1.42981700	4.40183100	2.08485400
C	4.57871700	2.73822600	-0.78331300
H	5.46002400	2.22101800	-1.15220600
C	-5.15924900	-1.20932000	-2.25082200
H	-5.83250300	-0.61321300	-2.86115400
C	-4.87236600	-2.52945300	-2.60751100
H	-5.32175000	-2.96338400	-3.49667600
C	-3.44694900	3.67810000	0.34109600
H	-3.13597700	4.71860900	0.22877300
H	-4.25535300	3.62308100	1.07213100
H	-3.82382100	3.33014900	-0.62520500
Ni	-0.15877200	0.01186700	0.21410300
C	0.20553700	-1.46826600	1.36912800
C	-0.19081900	-1.36473800	2.71942500
C	0.21931500	-2.76154300	0.79706300
C	-0.62198500	-2.48081900	3.44128600
H	-0.17259200	-0.40054100	3.21984800
C	-0.20334900	-3.87345000	1.52285100
H	0.53840000	-2.88611900	-0.23132200
C	-0.63192300	-3.74458400	2.84944200
H	-0.93495500	-2.35921600	4.47609800
H	-0.19299100	-4.85181800	1.04756700
H	-0.94891500	-4.61669900	3.41468900
Br	-0.21774200	-0.68401400	-2.15809900
H	-0.41467300	3.57044000	-2.91847600
H	0.51409700	4.74951200	-1.94428600
H	-5.15174600	-0.36220200	1.65908700
H	-3.90652300	-0.33672200	2.94600100
C	1.80654400	-0.26129300	1.03768300
H	2.00797500	0.16271300	0.04758900
C	1.92348300	0.80920000	2.12406400
H	2.90225600	1.29896300	2.04761500

H	1.16261400	1.58757400	2.02799600
H	1.86787400	0.35749400	3.11493100
C	2.82417200	-1.35641300	1.29989400
C	3.46660000	-2.10883300	0.16801400
C	3.10967700	-1.95715200	-1.18010900
C	4.50599700	-2.99508100	0.50162800
C	3.77915000	-2.67981000	-2.17024200
H	2.28394300	-1.31725800	-1.47538400
C	5.17700300	-3.70708700	-0.48716800
H	4.76788600	-3.10315000	1.54873300
C	4.81540500	-3.54980400	-1.82961300
H	3.47975900	-2.56269400	-3.20828500
H	5.98072800	-4.38665200	-0.21519400
H	5.33698400	-4.10736800	-2.60371300
O	3.18942400	-1.57725900	2.44955000



TS-RR'

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N	-2.29455900	-0.06761100	0.70902700
C	-1.64022700	2.71299000	0.19518200
C	1.48183300	3.18971300	-0.99475600
C	3.13156300	4.43841800	0.27753200
H	3.36903400	5.12870400	1.08251300
C	-2.94740200	0.87882000	1.27689500
C	1.80490400	4.08207800	0.03735200
H	1.01743500	4.49960400	0.66189300
C	-3.66336300	-1.80381200	-0.43650600
C	-0.90649300	4.02046600	-1.48225500

C	-3.12828500	-2.93415500	-1.06306600
H	-2.28426500	-3.44676900	-0.60961700
C	0.04391600	2.81037200	-1.29221600
H	0.02678400	2.15226800	-2.16350300
C	-3.07851500	-1.32997000	0.88149200
H	-2.39683600	-2.08628900	1.27028200
C	4.15321700	3.90697900	-0.51465800
H	5.18708400	4.18264700	-0.32623800
C	-4.11482400	-0.91724100	1.95067000
C	2.51164600	2.66211600	-1.78328900
H	2.26772900	1.95637700	-2.57285600
C	-2.61192400	2.35909100	1.31253900
C	-3.65817100	-3.38935500	-2.27173200
H	-3.22985900	-4.26540100	-2.75043800
C	-4.73324000	-1.13025700	-1.04251400
H	-5.15752600	-0.24505700	-0.57245000
C	-1.94302300	2.67778300	2.68101400
H	-1.02277400	2.10453000	2.81857900
H	-2.63562300	2.43526600	3.49217800
H	-1.70385600	3.74462200	2.73618300
C	3.84108600	3.01869900	-1.54446800
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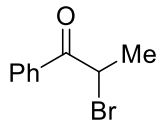
C	-5.26327700	-1.58419300	-2.24949200
H	-6.09333800	-1.05414300	-2.70901700
C	-4.72704100	-2.71783900	-2.86567900
H	-5.13899100	-3.07181900	-3.80683800
C	-3.91708100	3.17979600	1.17666800
H	-3.69187200	4.24648900	1.23206100
H	-4.60029100	2.91654600	1.98580400
H	-4.41548700	2.98597100	0.22246000
Ni	-0.35639800	-0.03660700	0.10134200
C	0.16984200	-1.64726100	1.09733800
C	-0.04722900	-1.71360900	2.48867500
C	0.56122500	-2.84579200	0.47198100
C	0.11262400	-2.89615800	3.21845200
H	-0.34337000	-0.81730200	3.03799800
C	0.72281200	-4.03692600	1.18792800
H	0.75062900	-2.84807300	-0.59820900

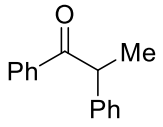
C	0.49728700	-4.06875700	2.56561100
H	-0.05492200	-2.89976100	4.29394500
H	1.03139700	-4.94160900	0.66762200
H	0.62898600	-4.99181200	3.12514500
Br	-0.02970300	-0.54049200	-2.25164100
H	-1.44489200	4.00018600	-2.43296000
H	-0.41777500	4.98797500	-1.35600700
H	-5.13858500	-1.20962200	1.71720800
H	-3.84584100	-1.25902300	2.95431800
C	2.43352100	0.39083800	1.22394600
H	2.34659600	0.78930900	0.21944100
C	1.98166200	1.22533800	2.37671100
H	2.79682700	1.88815800	2.70852600
H	1.13672700	1.86448800	2.10676600
H	1.72640800	0.59505400	3.23343000
C	3.36307700	-0.69470400	1.48672900
C	4.02261200	-1.42574300	0.35279600
C	3.54990700	-1.39141600	-0.96752900
C	5.17095700	-2.17835900	0.64582200
C	4.22011700	-2.09020700	-1.97307700
H	2.63721300	-0.86103900	-1.21918800
C	5.84437700	-2.86626500	-0.36005100
H	5.51400100	-2.20809700	1.67487000
C	5.37107900	-2.82221500	-1.67531400
H	3.83174600	-2.06748600	-2.98790700
H	6.73638600	-3.44004900	-0.12093900
H	5.89326100	-3.36215100	-2.46149200
O	3.67533700	-0.96005100	2.65932800



R–Br singlet

C	2.31857800	1.07276300	-0.51045600
C	3.58143700	0.48969600	-0.48215100
C	3.75932500	-0.76224600	0.11473300

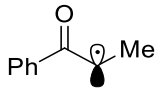
C	2.66879200	-1.42754400	0.67894900
C	1.40267700	-0.84395900	0.65328700
C	1.21545900	0.41486300	0.05964600
C	-0.10286900	1.11997100	0.01543700
O	-0.22959600	2.19204500	-0.55442700
H	4.42795200	1.00822800	-0.92369400
H	4.74507300	-1.21920900	0.13745500
H	2.80250800	-2.40406500	1.13574200
H	0.56285400	-1.38746200	1.07257700
H	2.15788500	2.04350900	-0.96742300
C	-1.31457700	0.51968400	0.74472400
C	-2.41533900	1.53082800	1.00310700
H	-1.01278800	0.00741200	1.65870400
Br	-2.01394200	-0.96117800	-0.41613700
H	-2.03920700	2.30573200	1.68252100
H	-3.28021900	1.04863500	1.46545300
H	-2.72021600	2.01775000	0.07521600



R–Ph singlet

C	2.84574900	0.55142600	0.74077300
C	3.90193700	-0.35430100	0.74590000
C	3.81252400	-1.53589600	0.00315700
C	2.66271100	-1.80512300	-0.74174900
C	1.60648500	-0.89387300	-0.75326800
C	1.68739500	0.29564500	-0.01242600
H	2.89130200	1.47237500	1.31262200
H	4.79497800	-0.14316400	1.32790500
H	4.63591800	-2.24530400	0.00718200
H	2.58668600	-2.72608800	-1.31325000
H	0.71345700	-1.12680300	-1.32279800
C	0.59474500	1.32325600	0.02137900
C	-0.63204000	1.16600600	-0.89519700
O	0.67336000	2.28067000	0.77903500

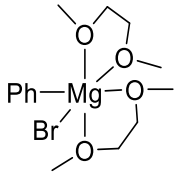
C	-1.28536300	2.53393300	-1.16064300
H	-2.15740500	2.41236200	-1.81124200
H	-0.57828600	3.21548600	-1.64585000
H	-1.60674500	2.99739600	-0.22492800
H	-3.24931800	-0.49240600	2.63869400
C	-2.96064100	-0.58924700	1.59532900
C	-3.52882000	-1.58843200	0.80200400
H	-4.26135400	-2.27150900	1.22345000
C	-3.14888100	-1.70376800	-0.53617400
H	-3.58607400	-2.47616300	-1.16366700
C	-2.20497100	-0.82652200	-1.07336900
H	-1.91817000	-0.91896500	-2.11917500
C	-1.62830000	0.17964400	-0.28661900
C	-2.01888100	0.28791300	1.05609800
H	-1.57963800	1.06138900	1.68032300
H	-0.29411900	0.75208000	-1.85272100



R• doublet

C	1.09953900	1.19308900	0.07785200
C	2.48026400	1.01792100	0.10787900
C	3.02541500	-0.26718600	0.03203500
C	2.18016800	-1.37301200	-0.07619100
C	0.79623800	-1.19753900	-0.09939500
C	0.23854400	0.08820600	-0.01855200
H	0.65759700	2.18263700	0.12697300
H	3.13379300	1.88245000	0.18870100
H	4.10314900	-0.40551200	0.05345900
H	2.59758600	-2.37392600	-0.14564100
H	0.15992200	-2.07118800	-0.20132200
C	-1.23985900	0.35978800	-0.04793000
C	-2.18202200	-0.72123500	0.12090600
O	-1.65157900	1.52649400	-0.19487000
C	-3.64944200	-0.49317400	0.07322700
H	-4.12006000	-1.12460300	-0.69483500

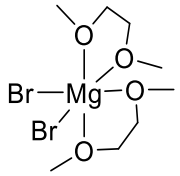
H	-3.86645000	0.55581800	-0.13785400
H	-4.12179600	-0.77239500	1.02699600
H	-1.82418000	-1.72637400	0.32349600



***cis*-PhMgBr(dme)$_2$ singlet**

Mg	0.20688600	-0.06047100	0.00065800
Br	1.15543100	-2.41928600	-0.34736900
C	3.02856800	0.05688300	1.30792600
C	2.14405600	0.44803500	2.47779900
O	2.47556800	0.63934000	0.12351600
O	0.78921000	0.21040300	2.10814100
H	2.41194800	-0.16030700	3.35219400
H	2.26935400	1.50862000	2.74166500
H	4.04782200	0.43598400	1.47337900
H	3.05216000	-1.03221500	1.18887800
C	-0.54476900	1.69008500	-2.41266000
C	0.11595100	2.76010500	-1.57089000
H	-0.49939800	1.97610200	-3.47323600
H	-1.59229200	1.55819900	-2.11469900
H	-0.44206200	3.70318300	-1.66937000
H	1.15186700	2.93369200	-1.90029400
O	0.10378800	2.32055200	-0.21914100
O	0.16729100	0.46839900	-2.20862800
C	-0.31549200	-0.58585100	-3.06230300
H	-1.37984100	-0.76472200	-2.87347000
H	-0.15660600	-0.30547400	-4.11146200
H	0.25624700	-1.47588000	-2.80259600
C	0.64164300	3.27575400	0.68351800
H	1.70632900	3.45424700	0.48208700
H	0.09054900	4.22336900	0.61220500
H	0.52228100	2.86363900	1.68545000
C	-0.12769700	0.16639800	3.20578000

H	0.12821300	-0.66362100	3.87526100
H	-0.10145200	1.11229500	3.76380600
H	-1.11479600	0.01263300	2.77026900
C	3.29425700	0.37798800	-1.02429800
H	2.77912600	0.81072100	-1.88192600
H	4.27713300	0.85105200	-0.89558700
H	3.40014500	-0.70132800	-1.17380100
C	-1.94516400	-0.16187600	0.26797400
C	-2.81808900	0.93605800	0.45821400
C	-2.58855100	-1.42332800	0.22929900
C	-4.20586300	0.80297400	0.59510700
H	-2.40429100	1.94597100	0.50227600
C	-3.97338200	-1.58085600	0.36070000
H	-1.98300300	-2.31961100	0.09090600
C	-4.79131000	-0.46344300	0.54485300
H	-4.82969500	1.68461600	0.74079200
H	-4.41574900	-2.57555300	0.32127000
H	-5.86851900	-0.57807700	0.64879600



***cis*-MgBr$_2$(dme)$_2$ singlet**

Mg	0.01424600	-0.04861300	-0.02865000
Br	-1.88706300	-1.60411200	0.61445700
C	-2.38877200	1.77108600	-0.56816900
C	-1.59002000	1.76930600	-1.85907000
O	-1.44772800	1.67662300	0.50462600
O	-0.76766100	0.59621200	-1.94292200
H	-2.25844500	1.82345500	-2.72564300
H	-0.91106600	2.62683700	-1.87833700
H	-2.96024300	2.70748200	-0.48320300
H	-3.07653500	0.91736300	-0.52205000
Br	1.90030500	-1.49482400	-0.87733600
C	2.10759800	1.02189000	1.86622700

C	1.77531200	2.23815500	1.01911300
H	2.41267900	1.33136500	2.87609600
H	2.90550100	0.42225400	1.41066300
H	2.65173900	2.88972600	0.92091800
H	0.96356000	2.80755600	1.48211900
O	1.30503500	1.83258300	-0.27047400
O	0.91233800	0.23696200	1.94397700
C	1.07307000	-0.95724100	2.73662700
H	1.85409400	-1.58889100	2.30195800
H	1.32531500	-0.67542100	3.76616600
H	0.11554600	-1.47652100	2.69797700
C	2.29439200	1.89281700	-1.30989800
H	2.63654300	2.92962500	-1.42306800
H	3.13245200	1.22283500	-1.10105300
H	1.80061000	1.55607800	-2.22044300
C	-1.26482200	-0.45153100	-2.80025200
H	-2.21313000	-0.84459400	-2.42272600
H	-1.37544600	-0.06068600	-3.81833100
H	-0.50847500	-1.23664400	-2.77614300
C	-2.08483400	1.69319700	1.78882600
H	-1.29033500	1.60250200	2.52964100
H	-2.61878200	2.64324400	1.92349900
H	-2.76740600	0.84343000	1.88446000

XI. References

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